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Chemoselective Electrophilic Oxidation of Heteroatoms by Hydroperoxy Sultams†

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The synthesis of novel hydroperoxy sultams **1b**−**d** and their potential as renewable chemoselective electrophilic oxidants for a wide range of nitrogen, sulfur, and phosphorus heteroatoms in nonaqueous media is described. Reactions of **1b**,**c** with secondary amines **10f,g** yielded the hydroxysultams **2b**,**c** and nitrone **11f** or radical **11g** depending on the substrate and stoichiometry, while tertiary amines **10a**−**d** gave amine oxides **11a**−**d**. Compounds **1c**,**d** oxidized various thioethers **12a**−**g** to sulfoxides **13a**−**g** smoothly that were isolated by chromatography in nearly quantitative yields. **1c** was regenerated from **2c** by treatment of the latter with acidified H_2O_2. Kinetic studies of the reaction of **1c** with 1,4-thioxane **12f** suggest that the reaction follows the second-order kinetics, first order in substrate and first order in oxidant with the second-order rate constant several orders of magnitude larger than that of the corresponding reaction with hydrogen peroxide and *tert*-butyl hydroperoxide without the need for any acid or heavy metal catalysts. The phosphines **14a**,**b** were also oxidized by **1c** to the respective phosphine oxides **15a**,**b** readily in quantitative yields. The reactions may be conducted at ambient temperature or lower and appear to proceed via a nonradical mechanism. Reactions are sensitive to steric as well as electronic factors.

Introduction

The chemo-, regio-, and stereoselective oxyfunctionalization of heteroatoms is an important area of oxidation chemistry.[1] Thus, to date, a number of oxidants have been developed to effect the selective oxidative transformation of N,[1f,2,3] S,[4] and P[1a] heteroatoms. However, for various reasons—selectivity, cost, efficiency, environmental constraints, etc.—the use of many reagents is restricted to specially favorable cases. Thus, the demand for suitable, cost-effective, and environmentally friendly selective oxidants with a wide range of application continues to increase to cope with the ever-growing complexity of chemical oxidations.[5]

Sultams such as Oppolzer's camphorsultam and toluene-2,α-sultam[6] are among the most reliable and widespread chiral auxiliaries for π-facial discrimination of various reactions, whereas the chiral N-sulfonyloxaziridines that are accessible by oxidation of respective *N*-sulfonylimines enjoy an important place in the stereoselective O-transfer reactions.[7] On the other hand, many cyclic and acyclic α-heterosubstituted hydroperoxides are also known to effect the selective electrophilic oxidation of various nucleophilic substrates. Prominent examples are the α-azohydroperoxides,[3d,e] perhydrates,[1b] 3-hydroperoxy-1,2-dioxolanes,[3e] 4a-hydroperoxyflavins,[4d] peroxyisoureas,[8]

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† Dedicated to Professor Dr. Peter Welzel on the occasion of his 65th birthday.

(1) (a) Hudlicky, M. *Oxidations in Organic Chemistry*; ACS Monograph 186; American Chemical Society: Washington, DC, 1990. (b) Adam, W.; Saha-Möller, C. R.; Ganeshpure, P. A. *Chem. Rev.* **2001**, *101*, 3498−3548. (c) Gilchrist, T. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 7, Chapter 6.1, pp 735−756. (d) Uemura, S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 7, Chapter 6.2, pp 757−787. (e) Kagan, H.; Luukas, T. In *Transition Metals for Organic Synthesis;* Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, Chapter 2, pp 361−373. (f) Murahashi, S.-I.; Imada, Y. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, Chapter 2, pp 373−383. (g) Kagan, H. B. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 327−356.

(2) *Hand book of Reagents for Organic Synthesis, Oxidizing and Reducing Agents*; Burke, S. D., Danheiser, R. L., Eds.; Wiley & Sons: Chichester, 1999.

(3) (a) Thellend, A.; Battioni, P.; Sanderson, W.; Mansu, D. *Synthesis* **1997**, 1387−1388. (b) Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1968**, *33*, 558−590. (c) Baumstark, A. L.; Chrisope, D. R. *Tetrahedron Lett.* **1987**, *28*, 1963−1966. (d) Vasquez, P. C.; Baumstark, A. L. *Adv. Oxygenated Processes* **1995**, *4*, 107−129. (e) Baumstark, A. L.; Chen, Y.-X.; Rodriguez, A. *J. Heterocycl. Chem.* **1996**, *33*, 1399−1402. (f) Larsen, J.; Jorgensen, K. A. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1213−1217. (g) Murray, R. W.; Singh; M. *Synth. Commun.* **1989**, *19*, 3509−3522.

(4) (a) Nakayama, J.; Nagasawa, H.; Sugihara, Y.; Ishii, A. *Heterocycles* **2000**, *52*, 365−382. (b) Gollnick, K.; Fries, S. *Angew. Chem.* **1980**, *92*, 849−850. (c) Eisch, J. J.; Behrooz, M.; Dua, S. K. *J. Organomet. Chem.* **1985**, *285*, 121−136. (d) Bruice, T. C.; Noar, J. B.; Ball, S. S.; Venkataram, U. V. *J. Am. Chem. Soc.*, **1983**, *105*, 2452−2463. (e) Murahashi, S.; Oda, T.; Masui, Y. *J. Am. Chem. Soc.* **1989**, *111*, 5002−5003. (f) Ali, M. H.; Stevens, W. C. *Synthesis* **1997**, 764−768. (g) Scettri, A.; Bonadies, F.; Lattanzi, A. *Tetrahedron*: *Asymmetry* **1996**, *7*, 629−633. (h) Boyed, D. R.; Sharma, N. D.; Haughey, S. A.; Kennedy, M. A.; McMurray, B. T.; Sheldrake, G. N.; Allen, C. C. R.; Dalton, H.; Sproule, K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1929−1933.

(5) Massa, A.; Lattanzi, A.; Siniscalchi, A. R.; Scettri, A. *Tetrahedron*: *Asymmetry* **2001**, *12*, 2775−2777 and references therein.

(6) (a) Kim, B. H.; Curran, D. P. *Tetrahedron* **1993**, *49*, 293−318. (b) Oppolzer, W.; Lienard, P. *Helv. Chim. Acta* **1992**, *75*, 2572−2582 and references therein.

(7) Davis, A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703−5742.

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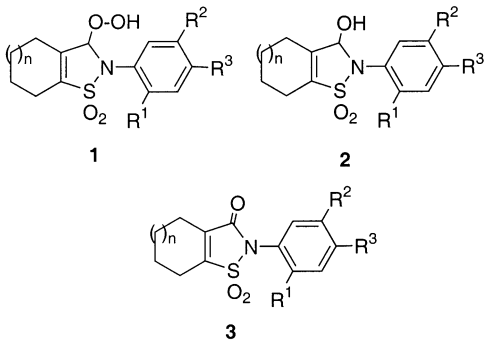
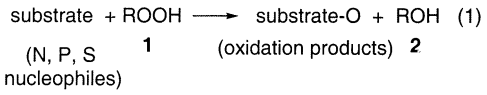
SCHEME 1



a: n = 1; $R^1 = R^2 = H$; R^3 = Br
b: n = 1; $R^1 = R^2 = H$; R^3 = *t*-Bu
c: n = 1; $R^1 = R^2$ = Cl; R^3 = *O*-*i*-Pr
d: n = 2; $R^1 = R^2$ = Cl; R^3 = *O*-*i*-Pr

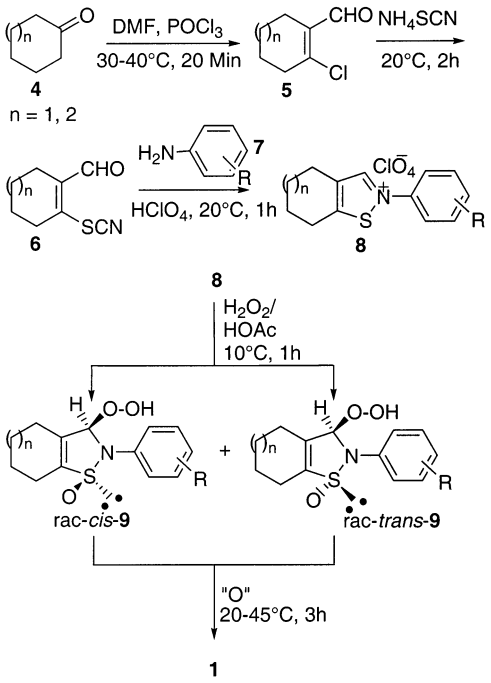
and peroxy acids.[9,10] α-Hydroperoxyamines are implicated as intermediates in the camphorsulfonylimine mediated enantioselective oxidation of sulfides by hydrogen peroxide.[11]

Recently, we have introduced a new class of chiral sultams of the type **1** (Scheme 1) that are characterized by a hydroperoxy group at the 3-position as stable crystalline compounds at room temperature and higher that are easily accessible in a few steps[12] and with a potential application as heteroatom oxidants (eq 1).



By inspecting structure of **1**, one may expect the peroxide oxygen atom to be electron deficient due to the strongly electron-withdrawing effect of the sulfone amide function adjacent to the hydroperoxy group. Furthermore, the electronic properties of the peroxide oxygen may be tuned by judicious variation of the substituents at the aromatic ring, thus potentially allowing one to predict the reactivity and selectivity of these reagents. In addition, this system offers even more important practical advantages: (1) high thermal stability; (2) in the solid-state lesser sensitivity to impact and to metals compared to H_2O_2, peracids, peresters, or TBHP, consequently safer to handle; (3) solubility in polar (MeOH) and nonpolar (CH_2Cl_2) solvents, thus more flexibility in solvent choice; (4) reactions are carried out under essentially neutral conditions; hence applicable to acid-sensitive substrates; (5) products may be separated directly by chromatography without the need of cumbersome workup procedures; (6) **1** may be regenerated by treatment of 3-hydroxysultam **2** with H_2O_2/HOAc mixture (vide infra); (7) no acid or heavy metal catalysts are needed; (8) the hydroperoxy sultams **1** are potential asymmetric oxidants.

SCHEME 2



Herein, we report (a) the syntheses of **1b**−**d**, **2c**,**d**, and **3c**,**d**[13] and the single-crystal X-ray structure of **1c**, (b) the use of these new class of oxidants as efficient reagents for the chemoselective electrophilic oxidation of a wide range of nitrogen, sulfur and phosphorus heteroatoms (eq 1), (c) the factors that are important in their application as selective oxidants, (d) comparison of their reactivity with those of the more common oxidants based on kinetic data, and (e) the scope and limitations of their use as selective oxidants together with a possible reaction mechanism.

Results and Discussion

The synthesis of some stable hydroperoxy sultams has been described previously.[12] Briefly, the commercially available ketones such as **4** are treated with the Vilsmeier reagent[14] in DMF and $POCl_3$ to give the β-chlorovinylaldehydes **5** in high yields. Subsequent reaction with NH_4SCN furnishes the thiocyanates **6** (Scheme 2).

The thiocyanates **6** react with suitably substituted anilines **7** in the presence of stoichiometric mounts of perchloric acid in glacial acetic acid by intramolecular cyclocondensation of the intermediate imines to the bicyclic isothiazolium salts **8** in a one-pot reaction at room temperature. Treatment of these salts with excess 30% H_2O_2 in glacial acetic acid gives **1** in high yields as crystalline products that are ready to use as oxidants.[15]

The choice of these oxidants for an oxidation reaction depends among other things on their yields, stability, solubility, and reactivity under the experimental condi-

(8) Majetich, G.; Hicks, R.; Sun, G.-r.; McGill, P. *J. Org. Chem.* **1998**, *63*, 2564−2573.
(9) Plesnicar, B. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 17, pp 521−584.
(10) Sawaki, Y. In *Organic Peroxides*; Ando, W., Ed.; Wiley: Chichester, 1992; Chapter 9, pp 425−477.
(11) Page, P. C. B.; Heer, J. P.; Bethell, D.; Collington, E. W.; Andrews, D. M. *Synlett* **1995**, *7*, 773−775.
(12) (a) Schulze, B.; Kirrbach, S.; Illgen, K.; Fuhrmann, P. *Tetrahedron* **1996**, *52*, 783−790. (b) Schulze, B. Obst, U.; Zahn, G.; Friedrich, B.; Cimiraglia, R.; Hoffman, H.-J. *J. Prakt. Chem. Chem. Ztg.* **1995**, *337*, 175−183.
(13) For **1a**, **2a**, and **3a**, see ref 12a.
(14) Arnold, Z.; Zemlicka, J. *Collect. Czech. Chem. Commun.* **1959**, *24*, 2385−2388.
(15) At lower temperatures (10−20 °C) and in shorter reaction times (1−2 h), the cis- or trans-configured cyclic hydroperoxy sulfin amides (sultims) **9** are isolated as solid products.

TABLE 1. Comparison of Bond Distances in Some O-Donors

compd	*d*(O−O) (Å)
HO−OH	1.464[a]
t-BuO−OH	1.480[a]
CH_3COO−OH	1.400[a]
CF_3COO−OH	1.400[a]
1	1.474

[a] Data from ref 17.

tions. For example, donor substituents at the aromatic ring reduce the hydroperoxide stability, whereas hydroperoxides with strongly electron-withdrawing groups may be prepared in good yields, but are virtually insoluble in common organic solvents. Therefore, we screened the hydroperoxides taking these problems into consideration and selected the hydroperoxides **1b**−**d** as oxidants and dichloromethane and chloroform as model organic solvents. Most reactions were run with **1c** since the yield of this compound was found to be the most satisfactory. The electrophilic character of the peroxy oxygen is further increased by the inductive effect of the chlorine atoms; the bulky isopropyloxy group would enhance the solubility in organic solvents. It must also be noted that in the absence of acid or metal catalysts divalent sulfur and trivalent nitrogen nucleophiles do not react readily with conventional alkyl hydroperoxides.[16]

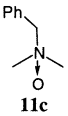
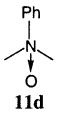
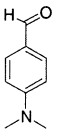
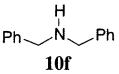
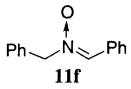
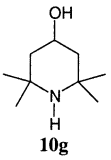
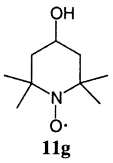
The remarkable stability also allowed us to obtain a single-crystal X-ray structure of this compound **1c** (Figure S1, Supporting Information). Selected bond distances and angles are presented in the Supporting Information.

Interestingly, the solid-state stability arises at least partly from the hydrogen bonding between the OH group of one molecule with a sulfone oxygen of a neighboring molecule leading to a polymer chain. Furthermore, the torsional angle between the aromatic ring and the approximate plane defined by the isothiazole ring is 85°. This leaves the peroxidic oxygen easily accessible to a potential nucleophilic substrate. The O−O bond distance of 1.474 Å (Table 1) is similar to that calculated for H_2O_2 and *tert*-butyl hydroperoxide, *t*-BuOOH, but significantly longer than that in peracetic acid, CH_3CO_3H, and trifluoroperacetic acid, CF_3CO_3H.[17]

Chemoselective Oxidation of Secondary and Tertiary Amines. The oxidation of tertiary amines to amine oxides is important since amine oxides themselves are often employed as selective O-transfer reagents. The results of oxidation of various secondary and tertiary amines **10** to amine oxides **11** is summarized in Table 2. The high yields of oxidation products is very unusual for hydroperoxy sultams **1** as secondary hydroperoxides because the normal reaction of a secondary hydroperoxide and dialkyl peroxides with α-hydrogen atoms with amines is base-catalyzed decomposition to form carbonyl compounds (see discussion below).

It is also clear from Table 2 that the reaction is sensitive to both steric and electronic factors. Sterically unhindered tertiary amines **10a**−**c** (entries 1−4) react

TABLE 2. Oxidation of Secondary and Tertiary Amines 10a−g with Hydroperoxy Sultams 1b,c

Entry	Amine	Oxidant (equiv.)	Solvent, T (°C), time (h)	Product	Yield (%)[a] 11	Yield (%)[a] 2
1	Et_3N **10a**	**1c** (2.3)	$CDCl_3$, 0-20, 0.75	$Et_3N\rightarrow O$ **11a**	95	77
2	 **10b**	**1b** (1.4)	$CDCl_3$, 20, 3.0	 **11b**	95	95
3		**1c** (2.5)	$CDCl_3$ 20, 3.0		95	75
4	 **10c**	**1b** (1.1)	$CDCl_3$, 33, 5.0	 **11c**	63	95
5	 **10d**	**1b** (1.1)	$CDCl_3$, 25, 10	 **11d**	37	58
6	 **10e**	**1c** (1.1)	$CDCl_3$, 25, 24	*b*	*b*	75[c]
7	 **10f**	**1c** (2.0)	$CDCl_3$, 0-25, 3.0	 **11f**	95	95
8	 **10g**	**1c** (2.1)	$CDCl_3$, 25, 24	 **11g**	74[d]	65[d]

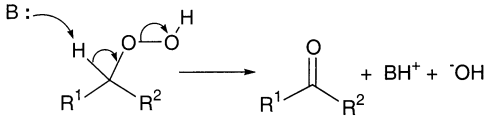
[a] Unless stated otherwise, calculated from NMR spectra using an internal standard (error = ±5% the stated values). [b] No conversion. [c] 25% **3c** was also detected. [d] Yield of isolated products based on conversion.

readily with hydroperoxides **1b**,**c** to the respective *N*-oxides **11** and the 3-hydroxysultams **2** in high yields. The fact that **10d** can be oxidized to **11d** whereas the similar compound **10e** (entry 6) does not react at all suggests that the hydroperoxide is acting as an electrophile: the electron density at this nitrogen atom is reduced due the electron-withdrawing CHO group at the 4-position of **10e**.

Instead, the reaction of **1c** is diverted to the more favorable decomposition to give **2c** and **3c** in a 4:1 ratio, respectively, leaving **10e** virtually intact. On the other hand, the lack of any reaction between **1c** and tribenzylamine (not in Table 2) after 24 h reflects the high sensitivity of the reaction to steric hindrance since this amine is not electron deficient. The reaction of a secondary amine with at least H-atom at α-C-atom, e.g., dibenzylamine **10f** (entry 7), normally gives the respective hydroxylamine with 1 equiv of an oxygen donor. Compound **10f** reacted to a mixture of the nitrone **11f** and the corresponding hydroxylamine with 1 equiv of **1c** while 2 equiv of oxidant reacted with **10f** to furnish **11f** in quantitative yield. The situation is different with the secondary amine that lacks a hydrogen atom on α-C. Thus, the NMR spectrum of the reaction mixture of the sterically hindered secondary amine **10g**, 4-hydroxy-

(16) Sheldon, R. A. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 16, pp 161−200.
(17) Yamaguchi, K.; Kazuhiro, K.; Takada, K.; Otsuji, Y.; Mizuno, K. In *Organic Peroxides*; Ando, W., Ed.; Wiley: Chichester, 1992; Chapter 1, pp 1−100.

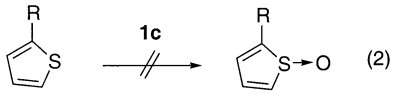
SCHEME 3



2,2,6,6-tetramethylpiperidine (TEMPOL-H), with **1c** after 24 h was too broad for quantitative analysis suggesting the formation of a radical. In fact, the EPR spectrum of this solution revealed a triplet signal with $a^N = 15.7$ G at $g = 2.007$, characteristic of the known nitroxide radical **11g**, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oyl (TEMPOL,)[18] that could be isolated by column chromatography in pure form and characterized by comparing the melting point with the literature values (entry 8). Its formation may be explained by further oxidation of the intermediate hydroxylamine to the corresponding amine oxide which reacts to form the resonance stabilized radical, similar to the corresponding reactions of hydrogen peroxide, peracids, and dimethyldioxirane with hindered amines.[19] Primary amines are very sluggish in their reaction with **1c**, while the reaction of pyridine with **1d** led to rapid base-catalyzed dehydration of the hydroperoxide to furnish the carbonyl compound **3d** in quantitative yield. This Kornblum−DeLaMare reaction[20] is not unexpected since it is well established that secondary hydroperoxides and dialkyl peroxides with hydrogen atoms attached to α- carbon are known to undergo similar base-catalyzed decomposition (Scheme 3) and may also explain why tertiary amines in Table 2 needed more than 1 equiv of oxidant for complete consumption.

Chemoselective Oxidation of Sulfides to Sulfoxides. The results of the oxidation of various sulfides to sulfoxides are summarized in Table 3.

The reaction of various sulfides **12** with **1c** is very smooth and is cleaner than that of amines **10** in Table 2. Also in this case, steric and electronic factors play a major role in determining the rate and the outcome of the reaction. Sterically unhindered aliphatic and aromatic sulfides **12a**,**b**,**d**−**g** are oxidized readily at 0−20 °C in excellent yields to the respective sulfoxides **13** in short reaction times. Allylphenyl sulfide **12b** (entry 3) and diallyl sufide **12e** (entry 6) were chemoselectively oxidized at S, and no traces of epoxides were detected by ^{1}H NMR spectroscopy. Further oxidation to sulfones was also not observed with all of the substrates in Table 3 even with more than 1 equiv of oxidant showing that the reaction is highly selective. However, when excess DMSO-d_6 was added to the hydroperoxide **1c**, rapid oxidation to sulfone took place as evidenced by ^{1}H and ^{13}C NMR spectroscopy. Interestingly, **12b** failed to react with **1c** in ethyl acetate even after 3 h at room temperature while reaction was complete within 2 h in dichloromethane. The relatively slow reaction of diphenyl sulfide **12c** is clearly due to steric grounds, while the absence of any reaction between the thiophene derivatives **12h**,**i** is almost certainly due to electronic reasons (eq 2).



(2)

12h:R = Me
12i: R = CHO

TABLE 3. Oxidation of Sulfides 12a−g with 1.0 Equiv of Hydroperoxy Sultams 1c,d

Entry	Sulfide	Oxidant	Solvent, T (°C), time(h)	Sulfoxide	Yield (%)[a] 13	2
1	Ph−S−CH$_3$ **12a**	**1c**	CH_2Cl_2, 20, 1.0	**13a**	95	90
2		**1d**	CH_2Cl_2, 20, 1.0		80	95
3	**12b**	**1c**	CH_2Cl_2, 20, 1.5	**13b**	98	85
4	Ph−S−Ph **12c**	**1c**	CH_2Cl_2, 20, 2.0	**13c**	86[b]	83[b]
5	PhCH$_2$-S-CH$_2$Ph **12d**	**1c**	$CDCl_3$, 0-20, 1.0	**13d**	98	92
6	**12e**	**1c**	CH_2Cl_2, 0, 0.75	**13e**	98	96
7	**12f**	**1c**	MeOH, 20, 1.0	**13f**	95	95
8	**12g**	**1c**	H_2O/ MeOH, 0-20, 4.0	**13g**	99[c]	99

[a] Yields refer to those of isolated, pure compounds. [b] Estimated from the ^{1}H NMR spectrum by using *s*-trioxane as the internal standard. [c] Sum of diastereomeric *S*-oxides.

In the case of **12h**, electrophilic attack at S would dramatically reduce the aromaticity (and thus the stability) of the 5-ring system. However, dimethyldioxirane is known to oxidize substituted thiophenes to the very unstable 1,1-dioxide products.[21] Similarly, the presence of the aldehyde group at position 2 in **12i** places a partial positive charge on S by resonance; again electrophilic attack is impeded. No oxidation of the aldehyde group is observed either. 1,4-Thioxane **12f** was quantitatively oxidized to the sulfoxide **13f** in methanol, suggesting solvent polarity is less important to the outcome and product yield.[22] Therefore, we became interested to know if substrates with low solubility in most organic solvents could also be oxidized under this system.

Thus, the oxidation of L-methionine **12g** in a mixture of water/methanol with hydroperoxide **1c** gave selectively a 1:1 diastereomeric mixture of *S*-oxides **13g** and the reduction product **2c** within 4 h in excellent yields. Oxidation took place exclusively at sulfur. All those products can be easily separated by column chromatography in pure form (see the Experimental Section).

(18) Baracu, I.; Dobre, V.; Niculescu-Duvaz, I. *J. Prakt. Chem.* **1985**, *327*, 667−674.
(19) (a) Toda, T.; Mori, E.; Murayama, K. *Bull Chem. Soc. Jpn.* **1972**, *45*, 1904−1908. (b) Toda, T.; Mori, E.; Higashida, S.; Murayama, K. *Bull Chem. Soc. Jpn.* **1972**, *45*, 636−638. (c) Murray, R.; Singh, M. *Tetrahedron Lett.* **1988**, *29*, 4677−4680.
(20) Kornblum, N.; DeLaMare, H. E.*J. Am. Chem. Soc.* **1951**, *73*, 880−881.
(21) Nagasawa, H.; Sugihara, Y.; Ishii, A.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1919−1926.
(22) However, see Dankleff, M. A. P.; Curci, R.; Edwards, J. O.; Pyun, H.-Y. *J. Am. Chem. Soc.* **1968**, *90*, 3209−3218.

TABLE 4. Oxidation at Phosphorus 14a−c with 1.0 Equiv of Hydroperoxy Sultam 1c

substrate	solvent, T (°C), time (h)	product	yield (%)[a] 15	2
$((H_3C)_2N)_3P$ **14a**	CH_2Cl_2, 0, 0.75	$((H_3C)_2N)_3P \rightarrow O$ **15a**	98	98
Ph_3P **14b**	CH_2Cl_2, 0, 0.75	$Ph_3P \rightarrow O$ **15b**	98	98
$Ph_3P \rightarrow S$ **14c**	acetone-d_6, 40, 24	**15b**	50	50

[a] Calculated from ^{1}H NMR spectra using an internal standard (error = ±5% of the stated values.

Chemoselective Oxidation of Phosphines to Phosphine Oxides. Although reduction of hydroperoxides with tertiary phosphines is no novelty,[23] phosphorus tris(dimethylamido)phosphine **14a** and triphenylphosphine **14b** were oxidized quantitatively even faster and at a lower temperature than the sulfur compounds **12** and the amines **10** to the respective phosphine oxides **15a** and **15b** in dichloromethane, whereas triphenylphosphine sulfide **14c**, a phosphine with a pentavalent phosphorus, reacted only slowly and at a higher temperature to **15a** in low yield (Table 4). The faster rate of oxidation of **14a**,**b** than **12** is in line with the greater nucleophilicity of phosphorus than sulfur.

Competitive Heteroatom Oxidations. To determine the relative nucleophilicities of sulfur and nitrogen centers toward the hydroperoxide **1c**, competitive experiments were carried out on equivalent amounts of dibenzylamine **10f** and dibenzyl sulfide **12d** by treatment with 0.5 equiv of the oxidant in deuterated chloroform at room temperature. After the end of the reaction, the ^{1}H NMR was recorded. Integration of the signals revealed that nearly all (> 99%) of the half equivalents of oxygen has been transferred to sulfur while virtually no reaction took place with **10f**. This finding is in a very good accord with the result observed with 2-sulfonyoxaziridines (Davis reagent) with **10f** and dibenzyl sulfide **12d** under the same experimental condition.[24] However, the spectrum of our reaction mixture did not show even traces of dibenzylhydroxylamine or dibenzyl sulfone.

Kinetic Studies. To gain more insight into the reaction mechanism, we carried out preliminary kinetic studies using oxidant **1c** and 1,4-thioxane **12f** based on the reported kinetic data for the oxidation of this sulfide with H_2O_2, *t*-BuOOH, and the hydroperoxyflavins in methanol.[25] The progress of the reaction was followed by iodometric titration. With [**12f**] = [**1c**], the plot of [**1c**]$^{-1}$ versus time is a straight line which means the reaction follows a second-order rate law (eq 3).

$$\text{rate} = \text{d[ROOH]}/\text{d}t = \text{d[sulfide]}/\text{d}t = -k\,[\text{sulfide}][\text{ROOH}] \quad (3)$$

The second-order rate constant k_2 of 3.6×10^{-2} M^{-1} s^{-1} was obtained from the slope of this plot (see Figure S2, Supporting Information). Under strictly pseudo-first-order conditions, [**12f**] ≥ 20 [**1c**], the rate was too fast to measure by iodometric titration. A linear relationship was established when the reaction was conducted in a thermostated flask at 30 °C using [**12f**]: [**1c**] of 3.01, 3.50, 5.06, and 7.58 molar ratios with the pseudo-first-order rate constants k_{obs} of 7.19×10^{-4}, 7.42×10^{-4}, 10.00×10^{-4}, and 14.60×10^{-4} s^{-1}, respectively. The linearity of the plot establishes that the reaction of **1c** with **12f** is first order in **1c** and first order in **12f**.

TABLE 5. Comparison of Second Order Rate Constants for the Reaction of 12f to 13f with Some Oxidants in Methanol at 30 °C

oxidant	k/M^{-1}s^{-1} (k_{rel})
t-BuOOH	3.75×10^{-6} (1)[a]
H_2O_2	9.38×10^{-5} (24)[a]
4a-FlCD$_3$OOH[b]	6.60×10^{-1} (1.8×10^5)[a]
1c	3.6×10^{-2} (9.6×10^3)[c]

[a] Data from ref 25. [b] 4a-Hydroperoxyflavin. [c] Determined by iodometric titration of the reaction mixture of **12f** and **1c**.

SCHEME 4

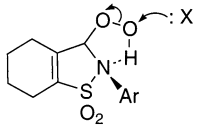


Table 5 shows comparison of published second-order rates for the reaction of **12f** with various oxidants.

Obviously, the rate of oxidation of **12f** with **1c** is nearly 4 orders of magnitude faster than that with *tert*-butyl hydroperoxide and more than 2 orders of magnitude than H_2O_2 under comparable experimental conditions.

Mechanism of Heteroatom Oxidations by Hydroperoxy Sultams. From the above results, it is possible to propose that heteroatom oxidation by hydroperoxy sultams may involve a polar transition state involving the typical S_N2 displacement by the incoming nucleophile at peroxide oxygen (Scheme 4) accompanied by rapid proton transfer to the oxygen atom adjacent to carbon. In addition to the sulfone amide functionality, intramolecular hydrogen bonding between the nitrogen atom and the peroxide hydrogen may account for the enhanced reactivity, as suggested for electrophilic nature of other α-hetero substituted hydroperoxides[1b,3d−f,4d,8] as well as organic peracids.[9,10] The mechanism and kinetic data presented here are closest to those reported for the cyclic α-azohydroperoxides. Although more mechanistic studies are necessary a similar mechanism may apply to the oxidation of phosphines and amines with hydroperoxy sultams as well.

Limitations. It has been shown that the reactions of hydroperoxy sultams with various N, S, and P nucleophiles give high yields of the oxidation products in short reaction times without any added catalyst or additives. However, these reactions are sensitive to steric as well as electronic factors. In reaction with amines, highly basic amines catalyzed decomposition of hydroperoxides competes with oxygen transfer to substrates. Reactions with pyridines lead to decomposition while primary amines were least reactive. Furthermore, the active oxygen content is lower than that of the more conventional oxidants, although this may not be limiting given the

(23) Horner, L.; Lurgeleit, W.; *Justus Liebigs Ann. Chem.* **1955**,*591*, 138−152. Poppas, J. J.; Keaveney, W. P.; Berger, M.; Rusch, R. V. *J. Org. Chem.* **1968**, *33*, 787−792.

(24) Zajac, Jr., W. W.; Walters, T. R.; Darcy, M. G. *J. Org. Chem.* **1988**, *53*, 5856−5860.

(25) Kemal, C.; Chan, T. W.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 405−409.

possibility to recycle the hydroxy sultam **2c** in one step to the active oxidant **1c** in good yield (see the Experimental Section).

Conclusion

In summary, we have shown that stable hydroperoxy sultams possess an attractive monooxygen donation capacity as *recyclable* mild reagents for a wider range of heteroatom oxidations without the need to employ acid or heavy metal catalysts in non aqueous media. The base-catalyzed decomposition of hydroperoxides observed with some amines may be minimized by lowering the reaction temperature and is completely absent in the reaction with the nonbasic nucleophiles sulfides and phosphines. The kinetic studies in methanol of the oxidation of **12f** with **1c** showed that the reaction is first order in both the oxidant and the substrate and the rate is much faster than oxidation of **12f** with H_2O_2 or *t*-BuOOH under comparable experimental conditions. The use of the sultam skeleton holds several advantages. The hydroxysultam byproducts **2c**,**d** can be recycled to **1c**,**d**. Furthermore, the sultam skeleton can in principle be modified to afford an effective chiral oxidant. Extensive efforts are currently underway in our laboratory to better understand the mechanism and to extend applications of these compounds to other substrates.

Experimental Section

General Methods. Melting points were corrected. Microanalyses were performed by the Microanalysis Service of the University of Leipzig. ^{1}H and ^{13}C NMR spectra were recorded on the δ scale (ppm) in $CDCl_3$, acetone-d_6, or D_2O solvents at 200 or 300 MHz (^{1}H) and at 50 or 75 MHz (^{13}C) against residual solvent signals as references. An FTIR spectrophotometer was used for the IR spectra (KBr pellets). UV/vis spectra were recorded on a spectrometer. A 70 eV equipment was used for the MS spectra. TLC analyses were conducted on precoated plates (silica gel 60 F $_{254}$), and the pots were visualized either by UV irradiation at 254 nm or by spraying with a saturated solution of KI in acetic acid. Silica gel (0.063−0.200 mm) was used for flash chromatography. All starting amines, phosphines, and sulfides and the ketones **4** are commercial products and were used without further purification. Compounds **5**,[14,26] **6**,[27] and **8b**−**d**[12] were prepared analogous to the reported procedure. A sample of the aniline **7c** was kindly supplied by the Bayer AG. Solvents were dried by standard methods and purified by distillation before use. All oxidation products **11a**,[28] **11b**−**d**,[29] **11f**,[30] **11g**,[31] **13a**−**c**,**f** [32] **13d**,[33] **13e**,[34] **13g**,[35] **15a**,[28] and **15b**[36] are known and gave the reported spectral data.

CAUTION: Although we have not encountered a single incident over the years, peroxides should always be considered potentially explosive and thus hazardous. In fact, more care should be exercised in handling perchlorates and 30% H_2O_2 than any of the new hydroperoxides reported here.

General Procedure for the Preparation of Hydroperoxy Sultams 1. The hydroperoxy sultams **1b**−**d** were prepared by treatment of the respective isothiazolium salts **8** (0.5 mmol) with excess 30% H_2O_2 (2.5 mL) in glacial acetic (3 mL) at room temperature (**1b**, 2 h) or at 45 °C (**1c**,**d**, 4 h) following the general procedure developed for the synthesis of **1a**.[12a]

2(4-*tert*-Butylphenyl)-3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (1b): yield 0.23 mmol, 46%;[37] mp 132−135 °C; FT-IR (KBr) 1516, 1363, 1270, 1220, 1155, 1070 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 224 (3.90), 267.0 (2.87); MS (EI) *m*/*z* 319.3 (M − H_2O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.82 (m, 4H), 2.51 (m, 4H), 5.84 (s, 1H), 7.36−7.43 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.1, 21.4, 21.5, 23.4, 31.8, 35.0, 92.5, 123.5, 127.2, 132.1, 137.2, 140.1, 150.2.

2(2,5-Dichloro-4-isopropyloxyphenyl)-3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (1c): yield 0.38 mmol, 75%; mp 195−197 °C; FT-IR (KBr, cm^{-1}) 3413, 1483, 1376, 1294, 1221, 1159, 1091 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 239 (4.09), 285 (3.31), 290 (3.31); MS (EI) *m*/*z* 407.1 (M − 1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40 (d, J = 5.8.0 Hz, 6H), 1.80−1.90 (m, br, 4H), 2.20−2.60 (m, br, 4H), 4.56 (m, 1H), 5.67 (s, br, 1H), 7.04 (s, 1H), 7.64 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.2, 21.3, 22.1, 23.2, 73.0, 94.3, 116.1, 123.2, 123.4, 134.1, 134.8, 137.1, 140.1, 155.3. Anal. Calcd for $C_{16}H_{19}Cl_2NO_5S$ (408.29): C, 47.09; H, 4.66; N, 3.43; Cl, 17.38; O, 19.61. Found: C: 46.60; H, 4.67; N, 3.33; Cl, 17.31; O, 19.70.

2(2,5-Dichloro-4-isopropyloxyphenyl)-3-hydroperoxy-2,3,5,6,7,8-hexahydro-4*H*-cyclohepta[*d*]-isothiazole 1,1-dioxide (1d): yield 0.4 mmol, 80%; mp 200−203 °C; FT-IR (KBr, cm^{-1}) 1484, 1377, 1292, 1224, 1157, 1080 cm^{-1}; ^{1}H (200 MHz, $CDCl_3$) δ 1.41 (d, J = 6.0 Hz, 6H), 1.70−1.90 (m, 6H), 2.40−2.72 (m, 4H), 4.58 (m, 1H), 5.58 (s, 1H), 7.05 (s, 1H), 7.58 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ 22.0, 23.9, 25.9, 26.7, 28.3, 30.3, 73.0, 94.5, 116, 123.5, 134.0, 134.7, 139.3, 142.5, 155.3.

Chemoselective Oxidation of Secondary and Tertiary Amines 10a−g with Hydroperoxy Sultams 1b,c. General Procedure. A 1.1−2.5 equiv portion of the hydroperoxides **1b**,**c** (97−98% pure by iodometric assay) was dissolved in the appropriate solvent (Table 1) and treated with the amine at 0 °C (ice cooling). The temperature was raised, and the mixture was stirred for the specified times. The progress of the reaction was monitored by TLC (ethyl acetate/*n*-hexane 4:5; saturated KI in acetic acid): When the reaction was finished, the crude mixture was analyzed by ^{1}H NMR spectroscopy after addition of an internal standard. All amine oxide products are known and gave satisfactory ^{1}H and ^{13}C NMR analyses. Compounds **2b**,**c** were characterized in the crude mixture by comparison of their NMR spectra with those of independently prepared compounds (see below and the Supporting Information). In case of the reaction of 0.127 mmol of **10g** with 0.142 mmol of **1c**, the reaction was incomplete after 24 h. The crude product was purified by silica gel chromatography (ethyl acetate/*n*-hexane 4/5 (vol/vol) and then ethyl acetate/methanol 1/1 (vol/vol)) to yield **11g** (0.047 mmol, 74%) and **2c** (0.061 mmol, 65%), respectively. In cases where significant decomposition occurred in competition with oxygen transfer from **1c** at room temperature, the corresponding compound **3c** was identified by comparison of TLC and NMR data with those of independently prepared **3c** (Supporting Information). When the amine was pyridine, base-catalyzed dehydration of **1d** (0.112 mmol) to the carbonyl compound **3d** had occurred at 70 °C within 6h while

(26) Reddy, C. P.; Tanimoto, S. *Synthesis* **1987**, 575−577.
(27) (a) Mühlstädt, M.; Brämer; R.; Schulze, B. *Z. Chem.* **1976**, *16*, 49−51. (b) Schulze, B.; Brämer; R.; Kleinpeter, E.; Mühlstädt, M. *J. Prakt. Chem.* **1976**, *318*, 795−800.
(28) Bravo, R.; Laurent, J.-P. *J. Chem. Res., Synop.* **1983**, 61.
(29) Ferrer, M.; Sanchez-Baeza, F.; Messeguer, A. *Tetrahedron* **1997**, *53*, 15877−15888.
(30) Murray, R.; Singh, M. *J. Org. Chem.* **1990**, *55*, 2954−2957. Murray, R.; Singh, M. *Tetrahedron Lett.* **1988**, *29*, 4677−4680.
(31) Kluge, R.; Schulz, M.; Liebsch, S. *Tetrahedron* **1996**, *52*, 5773−5782.
(32) Hashmat Ali, M.; Stevens, W. C. *Synthesis* **1997,** 764−765.
(33) Yang, R.-Y.; Dai, L.-X. *Synth. Commun.* **1994**, *24*, 229−236.
(34) Block, E.; Zhao, S. H. *Tetrahedron Lett.* **1990**, *31*, 5003−5006.
(35) (a) Holland, H. L.; Andreana, P. R.; Brown, F. M. *Tetrahedron*: *Asymmetry* **1999**, *10*, 2833−2843. (b) Holland, H. L.; Brown, F. M. *Tetrahedron*: *Asymmetry* **1998**, *9*, 535−538.
(36) (a) Cantrill, A. A.; Osborn, H. M. I.; Sweeney, J. *Tetrahedron* **1998**, *54*, 2181−2208. (b) Aitken, R. A.; Karodia, N. *Eur. J. Org. Chem.* **1999**, 251−254.

(37) Unlike **1c**,**d** which require almost no further purification, this product is usually contaminated with its hydroxy derivative **2b** and/or the keto compound **3b** that need to be separated by column chromatography.

no reaction was observed at room temperature. Compound **3d** was isolated in quantitative yield (0.111 mmol, 99%) by removal of the unreacted pyridine and the water under reduced pressure.

2-(2,5-Dichloro-4-isopropyloxyphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (3d): mp 130−134 °C; FT-IR (KBr) 1734, 1483, 1377, 1331, 1230, 1170, 1099 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 230 (4.16), 232 (4.15), 284 (3.37), 291 (3.35); MS (EI) *m*/*z* 403.1 (M − 1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, J = 6.0 Hz, 6H); 1.78 (m, 2H), 1.90 (m, 4H), 2.75 (m, 2H), 2.85 (m, 2H), 4.62 (m, 1H), 7.11 (s, 1H), 7.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 24.3, 24.9, 25.8, 26.5, 30.0, 73.0, 116.0, 118.0, 123.2, 132.9, 134.3, 138.5, 148.9, 156.1, 159.0.

Chemoselective Oxidation of Sulfides12a−f to Sulfoxides 13f−g. General Procedure. A 0.1−1.0 mmol portion of **1c**,**d** dissolved in the appropriate solvent (Table 2) was dropped via a syringe to a solution of 1.0 equiv of the respective sulfides **12a−f** at 0 °C (ice cooling) under N_2. The cooling was removed, the temperature raised as indicated, and the mixture was stirred for the specified time. The progress of the reaction was monitored by TLC. When the reaction was finished, the crude mixture was analyzed by ^{1}H NMR spectroscopy after addition of an internal standard. Isolation of the pure sulfoxides **13** and the hydroxy compounds **2** was achieved by silica gel chromatography (ethyl acetate/*n*-hexane 4/5 (v/v); saturated KI in acetic acid) following solvent removal from the mixture under reduced pressure.

2-(2,5-Dichloro-4-isopropyloxyphenyl)-3-hydroxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (2c): mp 148−150 °C; FT-IR (KBr) 3430, 1485, 1375, 1296, 1223, 1159, 1093 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 238 (4.00), 285 (3.21), 291 (3.21); MS (EI) *m*/*z* 391.1 (M − 1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 (d, J = 6.0 Hz, 6H), 1.80−1.90 (m, br, 4H), 2.15−2.60 (m, br, 4H), 4.58 (m, 1H), 5.49 (s, br, 1H), 7.05 (s, 1H), 7.53 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.0, 21.4, 22.2, 23.4, 73.1, 84.4, 116.5, 122.6, 123.1, 134.98, 135.03, 143.1, 155.2.

2-(2,5-Dichloro-4-isopropyloxyphenyl)-3-hydroxy-2,3,5,6,7,8-hexahydro-4*H*-cyclohepta[*d*]isothiazole 1,1-dioxide (2d): mp 204−207 °C; FT-IR (KBr) 3372, 1485, 1375, 1280, 1223, 1155, 1057 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 238 (3.56), 284 (2.92), 316 (2.29); MS (EI) *m*/*z* 405.1 (M − 1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40 (d, J = 6.0 Hz, 6H), 1.70−1.90 (m, 6H), 2.5−2.70 (m, 4H), 3.21 (d, J = 10.6 Hz, 1H), 4.57 (m, 1H), 5.42 (d, J = 10.6 Hz,1H), 7.05 (s, 1H), 7.54 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.0, 23.7, 26.4, 26.8, 28.8, 30.3, 73.0, 84.3, 116.0, 122.9, 123.1, 134.7, 134.8,137.3, 145.5, 155.1. Anal. Calcd for $C_{17}H_{21}Cl_2NO_4S$ (406.32): C, 50.25; H, 5.21; N, 3.45. Found: C, 50.30; H, 5.30; N, 3.40.

Chemoselective Oxidation of Methionine 12g to Methionine S-Oxide 13g. A 165 mg (0.404 mmol) portion of hydroperoxide **1c** dissolved in 10 mL of methanol was dropped within 20 min via a syringe to a solution of the 60 mg (0.403 mmol) of L-methionine **12g** in distilled water at 0 °C (ice-cooling) under N_2. An additional 10 mL of methanol was added, and the mixture was stirred at room temperature by which time the initially heterogeneous mixture became homogeneous as the reaction proceeded. The progress of the reaction was monitored by TLC (ethyl acetate/*n*-hexane 4/5; saturated KI in acetic acid; ninhydrin). When the reaction was complete, the solvent was removed under reduced pressure to dryness and replaced by 10 mL of distilled water. This mixture was extracted with ether (5 × 10 mL) until no trace of the hydroxy compound could be detected in the aqueous phase by TLC (silicagel 60, R_f 0.15, *n*-butanol/acetic acid/water 4/1/1 (v/v/v); ninhydrin). The combined ether phases were washed with 2 mL of water. The water phases were united and the water removed under reduced pressure until the weight of the flask remained constant to give 67 mg (99%) of white solid product. The ^{1}H NMR spectrum showed no resolution of the signals of diastereoisomers of **13g**. Baseline resolution of some signals could be achieved by ^{13}C NMR, which revealed that the product is approximately a 1:1 mixture of diastereoisomers. ^{1}H and ^{13}C NMR data are in full accord with the literature. The ether phase was washed with brine (2 × 5 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give 165 mg (98%) of pure hydroxysultam **2c**. Spectral data are as above.

Chemoselective Oxidation of Phosphines 14a−c to Phosphine Oxides 15a,b. The hydroperoxide **1c** (1 equiv), dissolved in the appropriate solvent (Table 5), was dropped via a syringe to a solution of the phosphines **14** at 0 °C (ice cooling) under N_2. The cooling was removed, the temperature was raised as indicated, and the mixture was stirred for the specified time. The progress of the reaction was monitored by TLC. When the reaction was finished, the crude mixture was analyzed by ^{1}H NMR spectroscopy after addition of an internal standard.

General Procedure for the Regeneration of 1c from 2c. A 65 mg (0.166 mmol) portion of **2c** was suspended in a mixture of 2 mL of glacial acetic acid and 2 mL of 30% hydrogen peroxide, and the suspension was stirred at 50 °C for 8 h. After the end of the reaction (monitored by TLC), the mixture was cooled to 5 °C, and the solid material was filtered over a sintered glass filter, washed with cold water (3 × 5 mL), and air dried to give 50 mg (0.122 mmol, 73% yield) of **1c** that has identical analytical data as above.

Competitive Oxidation of 10f and 12d. A 10.5 mg (0.049 mmol) portion of dibenzylamine **10f**, 9.7 mg (0.049 mmol) of dibenzyl sulfide **12d**, and 10 mg (0.025 mmol) **1c** were dissolved in deuteriochloroform at room temperature. After the end of the reaction (monitored by TLC), the ^{1}H NMR was recorded. Integration of the signals at δ 3.65, 3.83, 3.93, and 5.45 ppm that are, respectively, due to **12d**, **10f**, **13d**, and **2c** protons revealed that these products are present in the mixture nearly in 1:2:1:1 molar ratios in that order.

Kinetic Measurements. The oxidation of 1,4-thioxane **12f** to 1,4-thioxane oxide **13f** (Table 4, eq 3) was monitored by a modified iodometric titration[38] method of Kokatnur and Jelling on four samples containing 30.6 mg of hydroperoxide **1c** (0.073 mmol) in 10 mL of methanol and were thermostated at 30 °C after the addition of 1.00, 3.01, 3.50, 5.06, and 7.58 equiv of 1,4-thioxane. Reactions were followed to 75% completion. The corresponding rate constant of the 1:1 mixture was determined from the second-order plot while the apparent rate constants were determined from the pseudo-first-order plots. The precision of the constants is given in terms of the 95% confidence limit calculated with the "student t" test using the computer program ORIGIN.

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Supporting Information Available: Detailed characterization data (^{1}H and ^{13}C NMR, IR, MS) of **2b**, **3c**, and **8b−d**, ^{1}H and ^{13}C NMR spectra of **1b−d**, **2c**,**d**, **3c**,**d**, and **8c**,**d**. Figures S1,2. Complete X-ray crystallographic data for **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Kokatnur, V. R.; Jelling, M. *J. Am. Chem. Soc.* **1941**, *63*, 1432−1433.