(dd, J = 16.9 and 4.7 Hz, H), 2.61 (d, J = 16.9 Hz, H), 3.52 (dd, J = 9.8 and 6.3 Hz, H), 3.62 (dd, J = 9.8 and 1.7 Hz, H), 4.02 (m, H), 4.68 (m, H), 6.86 (s, H).

Anal. Calcd for $C_{17}H_{25}NO_7$: C, 57.46; H, 7.10. Found: C, 57.95; H, 7.16.

6a: IR (neat) 1685, 1592 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.35 (s, 9 H), 1.46 (br s, 3 H), 1.55 (br s, 3 H), 2.3–2.5 (m, 2 H), 3.50 (dd, J = 9.2 and 5.9 Hz, H), 3.79 (dd, J = 9.2 and 1.3 Hz, H), 3.84 (m, H), 4.40 (m, H), 5.18 (d, J = 5.9 Hz, H), 6.59 (d, J = 5.9 Hz, H); MS, calcd for $C_{15}H_{23}NO_5$ 297.1576, found 297.1568.

6b: IR (neat) 1779, 1690, 1630 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.33 (s, 9 H), 1.44 (br s, 3 H), 1.51 (br s, 3 H), 1.81 (s, 3 H), 2.43 (dd, J = 17.0 and 4.5 Hz, H), 2.56 (dd, J = 17.0 and 13.2 Hz, H), 3.46 (dd, J = 9.3 and 5.6 Hz, H), 3.76 (dd, J = 9.3 and 1.4 Hz, H), 3.85 (m, H), 4.46 (m, H), 6.80 (s, H); MS, calcd for $C_{17}H_{25}NO_7$ 355.1631, found 355.1615.

8 (major): IR (neat) 3460, 1690, 1620, 1592 cm^{-1}; NMR (C_6D_6, 60 °C) 1.38 (s, 9 H), 1.46 (br s, 3 H), 1.61 (br s, 3 H), 2.64 (br d, J = 4.9 Hz, 2 H), 2.95 (s, 3 H), 3.66 (dd, J = 8.1 and 5.7 Hz, H), 3.99 (m, H), 4.12 (dd, J = 8.1 and 2.1 Hz, H), 4.31 (m, H), 5.44 (d, J = 12.9 Hz, H), 7.45 (d, J = 12.9 Hz, H); MS, calcd for $C_{16}H_{28}NO_6$ (M + 1) 330.1916, found 330.1912.

9 (major): IR ($CHCl_3$) 1715, 1686 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.36 (s, 9 H), 1.49 (br s, 3 H), 1.58 (br s, 3 H), 2.13 (dd, J = 16.3 and 4.6 Hz, H), 2.30 (d, J = 16.3 Hz, H), 2.36 (m, 2 H), 3.03 (s, 3 H), 3.61 (dd, J = 8.8 and 5.9 Hz, H), 3.9 (m, H), 3.99 (dd, J = 8.8 and 1.3 Hz, H), 4.25 (m, H), 4.64 (dd, J = 4.7 and 1.4 Hz, H); MS, calcd for $C_{16}H_{28}NO_6$ (M + 1) 330.1916, found 330.1880.

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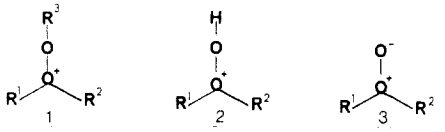
Registry No. **2**, 102308-32-7; **3a**, 54125-02-9; **3b**, 102308-33-8; **4a**, 102308-34-9; 4b, 102308-35-0; **5a**, 102308-36-1; **5b**, 102308-37-2; **6a**, 102308-38-3; **6b**, 102308-39-4; **8** (isomer 1), 102308-40-7; **8** (isomer 2), 102308-42-9; **9**, 102308-41-8; 4-methoxy-3-buten-2-one, 51731-17-0.

Communications

Oxygen Transfer by Dialkylperoxonium Ions

Summary: Oxygen-transfer from dialkylperoxonium ions R_2O^+OH has been demonstrated for three such species, where R_2 is a hydrocarbon chain or ring, by oxidation of several dialkyl sulfoxides, methyl phenyl sulfide, and the succinimide anion, with concurrent formation of the corresponding cyclic or bicyclic ether R_2O.

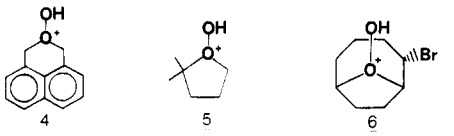
Sir: The formation of trialkylperoxonium ions **1** has been proposed in the Lewis acid induced ring closure of alkylperoxy bromides[1-3] and in the reaction of electrophiles with alkylperoxy alkenes.[4] Subsequent transformations of these intermediates has resulted in peroxy migration[1,3] or Baeyer–Villiger type O–O cleavage.[2,4]



Product studies of parallel reactions with hydroperoxy bromides and alkenes suggest the intermediacy of the corresponding dialkylperoxonium ions **2**.[3,4] However, further evidence is required to substantiate the existence of these ions and to confirm their suggested potential as oxygen-transfer reagents.[4]

The species **2** are structurally related not only to $H_3O_2^+$ but also to dioxygen ylides **3**, such as carbonyl oxides[5,6] and perepoxides,[7] and we anticipated that they might show oxygen-transfer chemistry of an intermediate nature.

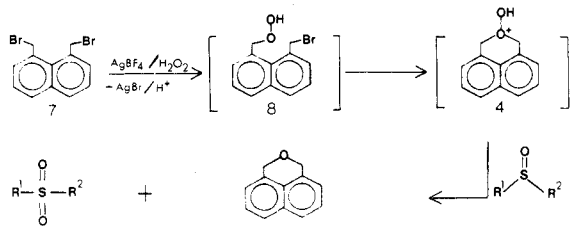
We now wish to report our preliminary findings on the oxygen-transfer capabilities of the three dialkylperoxonium ions, **4–6**.



Reaction of 1,8-bis(bromomethyl)naphthalene (**7**) with an excess of 85% hydrogen peroxide in diethyl ether, dried with $MgSO_4$, and silver tetrafluoroborate at 0 °C resulted in complete consumption of the dibromide and production of naphthopyran but in yields *no* greater than 45%. Upon incorporation of dialkyl sulfoxides, yields of naphthopyran could be increased up to 71%, with concurrent oxidation of the sulfoxide to sulfone (Scheme I). Although sulfone could arise from oxidation by $H_3O_2^+$, which can be present since acid is liberated during the formation of hydroperoxy bromide **8**, the *accompanying* increase in the yield of naphthopyran is consistent with the intermediacy of **4**. However, we sought stronger evidence for **4** through a *correlation* of sulfone and naphthopyran yields.

Thus, the reaction was carried out at room temperature for 90 s with 1, 2, or 3 mol equiv of benzyl methyl sulfoxide present and then quenched with triphenylphosphine to destroy excess hydrogen peroxide. The resultant products

Scheme I



$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Ph$; $R^1 = Me$, $R^2 = CH_2Ph$; $R^1 = R^2 = Ph$

(1) Bloodworth, A. J.; Bowyer, K. J.; Mitchell, J. C. *J. Org. Chem.* **1986**, *51*, 1790.
(2) Mitchell, J. C.; Heaton, S.; Porter, N. A. *Tetrahedron Lett.* **1984**, *25*, 3769.
(3) Porter, N. A.; Mitchell, J. C. *Tetrahedron Lett.* **1983**, *24*, 543.
(4) Bloodworth, A. J.; Courtneidge, J. L.; Eggelte, H. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1267.
(5) Adam, W.; Haus, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020.
(6) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832.
(7) Schaap, A. P.; Recher, S. G.; Faler, G. R.; Villasenor, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 1691.

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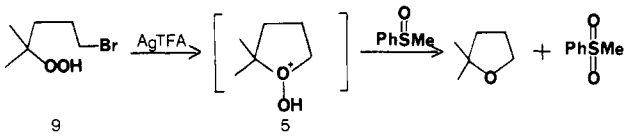
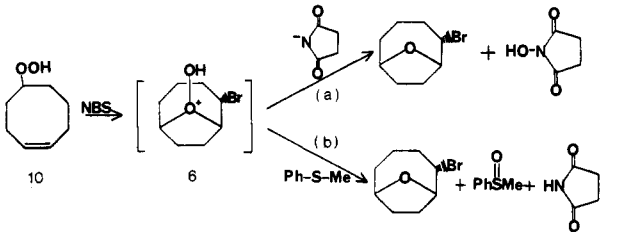
Scheme II



Scheme III



contained equimolar amounts of naphthopyran and sulfone, together with the appropriate amount (i.e., 0, 1, or 2 mol equiv) of unchanged sulfoxide. Furthermore, in an independent experiment it was shown that acidic hydrogen peroxide produces no substantial oxidation of the sulfoxide under these conditions.

These exact correlations provide compelling evidence for the formation of an intermediate which reacts with the sulfoxide to provide equimolar amounts of naphthopyran and sulfone. This, together with the associated trialkylperoxonium chemistry,[2] points firmly to structure **4**. The results also suggest that **4** may have a greater oxygen-transfer reactivity toward sulfoxides than does protonated hydrogen peroxide, but it is necessary to establish the respective concentrations of these two species before this can be confirmed.

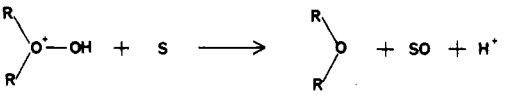
Further evidence for the existence and oxygen-transfer capability of species **2** came from the incorporation of methyl phenyl sulfoxide into the silver trifluoroacetate-mediated ring closure of 1-bromo-4-methyl-4-hydroperoxypentane (**9**). In the absence of sulfoxide, the cyclization product was 3,3-dimethyl-1,2-dioxane, which is believed to arise by a mechanism involving the peroxonium intermediate **5**.[3] With sulfoxide present, however, formation of the cyclic peroxide was completely suppressed, and the corresponding cyclic ether was obtained instead, together with an equimolar amount of sulfone (Scheme II). Treatment of the sulfoxide with acidic **9** under comparable conditions produced no appreciable amount of sulfone.

We have also demonstrated the viability of oxygen-transfer by intermediates resulting from electrophilic attack on 5-hydroperoxycyclooctene (**10**) (Scheme III).[8]

In this case, reaction of **10** with *N*-bromosuccinimide in *tert*-butyl alcohol cleanly afforded bicyclic ether and *N*-hydroxysuccinimide[4] (Scheme 3a), but when methyl phenyl sulfide was present, equimolar amounts of succinimide and methyl phenyl sulfoxide were obtained at the expense of *N*-hydroxysuccinimide (Scheme 3b). It was shown that neither starting hydroperoxide **10** nor *N*-hydroxysuccinimide produced oxidation of the sulfide under the same conditions. These results show that the bicyclic peroxonium ion **6** can efficiently transfer oxygen to suitable nitrogen- and sulfur-centered nucleophiles.

We believe that the results described herein for three different starting reagents, two different reaction types, and three different classes of oxidizable substrate, firmly establish the existence of dialkylperoxonium intermediates **2** and demonstrate their ability to participate in oxygen-transfer reactions (Scheme IV; S = oxidizable substrate).

Scheme IV



Little can yet be said about the nucleophilic vs. electrophilic character[9] and hence the selectivity of these new oxygen-transfer reagents. Yields of naphthopyran (Scheme I) were found to exhibit a small dependence upon the identity of the sulfoxide present and decreased along the series MeSOPh > PhSOPh > MeSOMe. The implied trend in sulfoxide trapping ability of **4** parallels that found for oxidations by perepoxide and carbonyl oxide intermediates, where it has been ascribed to nucleophilic character.[6,7,10] That **4** is more reactive than acidic hydrogen peroxide toward sulfoxides is a further indication of nucleophilic character. On the other hand, the reactions of **6** (Scheme III) show that dialkylperoxonium ions can be effective electrophilic oxygen-transfer reagents.

Clearly much more needs to be done to establish the position of these and other peroxonium ions within the existing spectrum of oxygen-transfer reagents and to establish the full range of substrates that may be oxidized by them. Work to this end is continuing in our laboratories.

Acknowledgment. We thank the S.E.R.C. for the award of an Earmarked Studentship.

(8) The isomeric bicyclo[3.3.1] peroxonium ion is also formed and exhibits parallel chemistry.

(9) DiFuria, F.; Modena, G. *Pure Appl. Chem.* **1982**, *54*, 1853.
(10) Ando, W.; Miyazak, H.; Kohmoto, S. *Tetrahedron Lett.* 1979, 1317.

A. J. Bloodworth,* T. Melvin
Department of Chemistry
University College London
London WC1H 0AJ, U.K.

John C. Mitchell*
Department of Chemistry
Royal Holloway and Bedford New College
University of London
Egham Hill
Surrey TW20 0EX, U.K.
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1,1′-Thiocarbonyldi-2,2′-pyridone. A New Useful Reagent for Functional Group Conversions under Essentially Neutral Conditions

Summary: 1,1′-Thiocarbonyldi-2,2′-pyridone is a useful reagent for the preparation of nitriles, carbodiimides, cyclic thionocarbonates, and isothiocyanates and deoxygenation of alcohols under essentially neutral conditions.

Sir: The development of efficient and reliable reagents for functional group conversions is a central objective of synthetic organic chemistry, and it is highly desirable that such conversions take place under mild conditions in the synthesis of complex molecules.

We now wish to report that 1,1′-thiocarbonyldi-2,2′-pyridone can be successfully utilized for various functional group conversions under essentially neutral conditions. In the course of studies on the synthetic utility of 2-pyridyl related active esters and carbonates,[1] we have found that

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