60 and 200 MHz. As previously, when isomers **9** and **10** were inseparable by VPC, the ratio of **9** to **10** was determined by preparative VPC collection and integration of appropriate segments in the NMR spectrum of the mixture.[9]

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(9) Satisfactory microanalytical data for alkoxy ketones **9** (from runs 3, 5, 6, 8, and 9) and **10** (from run 7) of Table I were provided.

Registry No. **3** ($R_1 = R_2 = Me$; $R_3 = R_4 = H$), 563-80-4; **3** ($R_1 = R_2 = R_3 = Me$; $R_4 = H$), 565-69-5; **3** ($R_1 = R_2 = Me$; $R_3 = Et$; $R_4 = H$), 7379-12-6; **3** ($R_1 = R_2 = Me$; $R_3 = i$-Pr; $R_4 = H$), 1888-57-9; **7a**, 1518-06-5; **7b**, 37010-00-7; **7c**, 69204-79-1; **7d**, 56829-66-4; **9** (R = H; R′ = Me), 36687-98-6; **9** (R = H; R′ = Et), 36687-99-7; **9** (R = H; R′ = *i*-Pr), 76916-70-6; **9** (R = R′ = Me), 10097-21-9; **9** (R = Me; R′ = Et), 76916-71-7; **9** (R = Me; R′ = *i*-Pr), 76916-72-8; **9** (R = Me; R′ = *t*-Bu), 76916-73-9; **9** (R = Et; R′ = Me), 76916-74-0; **9** (R = Et; R′ = *i*-Pr), 76916-75-1; **9** (R = *i*-Pr; R′ = Me), 76916-76-2; **9** (R = R′ = *i*-Pr), 76916-77-3; **10** (R = H; R′ = Me), 65857-35-4; **10** (R = H; R′ = Et), 76916-78-4; **10** (R = H; R′ = *i*-Pr), 76916-79-5; **10** (R = R′ = Me), 66508-06-3; **10** (R = Me; R′ = Et), 76916-80-8; **10** (R = Me; R′ = *i*-Pr), 76916-81-9; **10** (R = Me; R′ = *t*-Bu), 76916-82-0; **10** (R = Et; R′ = *i*-Pr), 76916-83-1; **10** (R = *i*-Pr; R′ = Me), 76916-84-2; **10** (R = R′ = *i*-Pr), 76916-85-3.

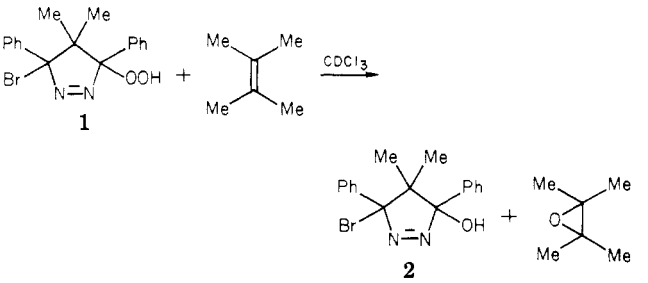
Communications

Epoxidation of 2,3-Dimethyl-2-butene by 3-Bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole

Summary: The uncatalyzed reaction of 2,3-dimethyl-2-butene and 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole produced tetramethylethylene oxide and 3-bromo-4,5-dihydro-5-hydroxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole in moderate yield.

Sir: The epoxidation of alkenes by hydroperoxides generally[1,2] requires the presence of a catalyst. For example, alkyl hydroperoxides, in the presence of Mo or V catalyst[1-3] or in contact with basic alumina,[4] will epoxidize alkenes. Recent reports indicate that certain olefins undergo direct epoxidation with such unusual hydroperoxides as triphenylsilyl hydroperoxide[4] and 2-hydroperoxyhexafluoro-2-propanol.[5] α-Substituted hydroperoxides,[6] furan endoperoxides,[7] and an intermediate in the metal ion catalyzed oxygenation of azibenzil[8] have also been reported to convert alkenes to oxiranes. The recent synthesis[9] of 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole (**1**) prompted us to investigate oxygen atom transfer reactions of this unstable[9] peroxide. We report the uncatalyzed reaction of 2,3-dimethyl-2-butene and **1** to produce tetramethylethylene oxide and 3-bromo-4,5-dihydro-5-hydroxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole (**2**).

2,3-Dimethyl-2-butene (3.4 mg, 0.040 mmol) was added (via syringe) to a cold solution of **1** (14.7 mg, 0.041 mmol) in 0.6 mL of $CDCl_3$ (Merck, no Me_4Si) in a 5-mm NMR tube. Reaction progress was determined by ^1H NMR spectroscopy. After complete disappearance of **1** ($t_{1/2} \simeq$ 45 min), monitored by the disappearance of the upfield methyl signal of **1** [δ −0.10 (s)], 54 ± 6% (average of two experiments) of 2,3-dimethyl-2-butene had been converted to tetramethylethylene oxide [δ 1.3 (s)]. Fifty percent of **1** had undergone reaction to produce **2** as evidenced by a new upfield signal at δ −0.05, while the remainder of **1** underwent decomposition via the reported thermal route.[9] Doubling the amounts of both reactants increased the yield of epoxidation to 67% (70% formation of **2**) with a half-reaction time of ca. 10–20 min. Tetramethylethylene oxide was collected by preparative VPC and shown to be identical with an authentic sample by comparison of spectral data as well as its acid-catalyzed conversion to pinacolone.



1 **2**

The pyrazoline, **2**, was isolated and characterized as follows. **1** (150 mg, 0.42 mmol) was added to 0.5 mL of 2,3-dimethyl-2-butene in 1.5 mL of cold $CDCl_3$. The mixture was agitated for several minutes to dissolve **1** and allowed to sit for 5 min. The solution was transfered to a clean, dry flask and the volatile components were removed under reduced pressure. The residue, recrystallized from $CDCl_3$/pentane, gave 55 mg (38% isolated yield) of pale yellow crystals of **2**: mp 93–94 °C dec; ^1H NMR ($CDCl_3$) δ −0.05 (s, 3 H), 1.7 (s, 3 H), 3.6 (s, 1 H), 7.3–7.8 (m, 10 H); IR (KBr) 3260 (br, OH), 3020, 2930 (w), 1520 (N=N, m), 1480 (m), 2382 (m), 1365 (m), 1220 (m), 1095 (m), 1070 (m), 1010 (m) cm^{-1}; peroxide test negative. Anal. Calcd: C, 59.14; H, 4.96; N, 8.11; Br, 23.15. Found: C, 59.27; H, 5.06; N, 8.11; Br, 23.02. Pure **2**, although considerably more thermally stable in $CDCl_3$ than **1**, underwent decomposition in 1 h at 22 °C with gas evolution. Products of this decomposition have not yet been characterized. **2** was stored at −20 °C as a solid with no decomposition noted after several weeks.

(1) (1) March, J. "Advanced Organic Chemistry", 2nd Ed., McGraw-Hill: New York, 1977; p 752.
(2) Swern, D. "Organic Peroxides"; Wiley Interscience: New York, 1971; Vol. II, p 83–86.
(3) (a) Mimoun, H.; de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37. (b) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295.
(4) Rebek, J.; McCready, R. *Tetrahedron Lett.* **1979**, 4337.
(5) Heggs, R. P.; Ganem, B. *J. Am. Chem. Soc.* **1979**, *101*, 2484.
(6) (a) Rebek, J., Jr.; McCready, R.; Wolak, R. *J. Chem. Soc., Chem. Commun.* **1980**, 705; (b) Rebek, J., Jr.; McCready, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602.
(7) Adam, W.; Rodriguez, A. *J. Am. Chem. Soc.* **1980**, *102*, 404.
(8) Ryang, H.-S.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 2129.
(9) Landis, M. E.; Lindsey, R. L.; Watson, W. H.; Zabel, V. *J. Org. Chem.* **1980**, *45*, 525.

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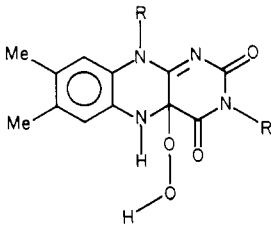
The reactivity of 1 toward 2,3-dimethyl-2-butene[10] compares well with that of 2-hydroperoxyhexafluoro-2-propanol[5] and appears to be greater than that of α-peroxy esters and nitriles.[6] The reactivity of 2-hydroperoxyhexafluoro-2-propanol can be rationalized[5] by structural similarities with peracids as well as the presence of electron-withdrawing substitutents. For α-peroxy esters, ketones, amides, and nitriles,[6] intramolecular hydrogen bonding similar to that in peracids[11] appears to account for the epoxidation reaction. Similarly, 1 can also be considered a peracid analogue. Intramolecular hydrogen bonding of the peroxy hydrogen in 1 to the ring nitrogen as well as the slightly electron-withdrawing substituents could then be the major factors for the increased reactivity of 1 as compared to that of alkyl hydroperoxides.

There are structural similarities between 1 and flavin 4a-hydroperoxides (3). Flavin 4a-hydroperoxides are



3

believed to be important intermediates in external flavoprotein monooxygenase activity[12] including bacteria bioluminescence.[13] Hamilton suggested[12a] that flavin 4a-peroxides undergo rearrangement to a carbonyl oxide intermediate (oxenoid[12a] intermediate) that would then be the oxygen-transfer agent in several monooxygenase reactions. A number of oxygen-transfer reactions have been suggested[6b,14] as model systems for these biochemical systems. The model system results[14c] of Bruice[15] have shown that flavin hydroperoxides are capable of oxidation of amines and sulfides. Preliminary results from 1 show that it will also readily oxidize amines and sulfides. It appears that 1 may mimic many of the reactions of flavin 4a-hydroperoxides. The reaction[16] of 1 with *N,N*-dimethylaniline or diphenyl sulfide produced 2 (50% isolated yield in both cases) and the corresponding amine oxide or sulfoxide in good yield. The amine oxide (isolated by crystallization) and the sulfoxide (isolated by preparative GC) were characterized by comparison of spectra with those of authentic samples. The reaction of 1 (0.1 M in $CDCl_3$) with diphenyl sulfide (5-fold excess) was complete within 10 min while the reaction of 1 and *N,N*-dimethylaniline, under similar conditions, was complete after 1 h.

Our data indicate that a hydroperoxide can be sufficiently reactive to effect oxygen-transfer chemistry without added catalysts to generate more reactive species. The reactions of 1 and similar peroxides[4-6] parallel those shown by flavin 4a-hydroperoxides[14,15] and suggest the continued study of these compounds as models for in vivo enzymatic monooxygenase activity.

We are continuing to investigate the oxygen-transfer properties of 1 to further evaluate 1 as a model for flavin systems.

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Registry No. 1, 76847-41-1; 2, 76847-42-2; 2,3-dimethyl-2-butene, 563-79-1; tetramethylethylene oxide, 5076-20-0.

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(10) Dialkyl olefins did not undergo epoxidation upon treatment with 1 (underwent normal thermal decomposition[9]). Enol ethers underwent reaction with 1 to produce 2 and a variety of epoxide rearrangement products.

(11) (a) Reference 1, pp 750–1. (b) Reference 2, p 472–5.

(12) (a) Hamilton, G. A. *Prog. Bioorg. Chem.* **1971**, *1*, 83–157. (b) Massey, V. Hemmerich, P. *Enzymes* **1976**, *12*, 191–252. (c) Bruice, T. C. *Prog. Bioorg. Chem.* **1976**, *4*, 1–87.

(13) Hasting, J. W. *CRC Crit. Rev. Biochem.* **1978**, 163.

(14) (a) Reference 5. (b) Keay, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 6876. (c) Ball, S.; Bruice, T. C. *Ibid.* **1980**, *102*, 6498 and references therein.

(15) (a) Iwata, M.; Bruice, T. C.; Carrell, H. L.; Glusker, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 5036 and references therein. (b) Ball, S.; Bruice, T. C. *Ibid.* **1979**, *101*, 4017.

(16) Inclusion of small amounts of *cis*-3-hexene[10] in the reaction mixture increased the isolated yields of 2 dramatically. 2 shows increased stability in the presence of olefins.

Photochemical Reaction of *N,N*-Dialkyl β,γ-Unsaturated Amides. Intramolecular Hydrogen-Transfer Reactions of Acyclic Olefins via Seven-Membered Cyclic Transition States

Summary: *N,N*-Dibenzyl and *N,N*-diallyl β,γ-unsaturated amides undergo cyclization on irradiation to give the corresponding pyrrolidin-2-ones via an unprecedented 1,6-hydrogen shift in acyclic olefins, while *N,N*-diethyl and *N,N*-diisopropyl β,γ-unsaturated amides are unreactive toward photolysis.

Sir: Photocyclization via intramolecular hydrogen transfer (e.g., type II cyclization) is one of the most important reactions in the photochemistry of ketones,[1] thioketones,[2] and olefins.[3] Recently, intramolecular hydrogen-transfer reactions of olefins have received considerable attention.[3,4] In the case of acyclic olefins these reactions are quite inefficient, and the inefficiency has been attributed to the presence of competitive processes such as cis–trans isomerization.[4] Thus, photocyclization of olefins via intramolecular hydrogen transfer has been limited to cyclic olefins. It is well-known that intramolecular hydrogen transfer through seven-membered cyclic transition states (1,6-hydrogen shift) is less favorable than that through six-membered ones (1,5-hydrogen shift) in acyclic systems.[5] Consequently, the photochemical 1,6-hydrogen shift of acyclic olefins has not yet been reported.[6]

(1) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(2) (a) Ho, K. W.; de Mayo, P. *J. Am. Chem. Soc.* **1979**, *101*, 5725. (b) Aoyama, H.; Suzuki, S.; Hasegawa, T.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1979**, 899.

(3) Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *101*, 5743 and references cited therein.

(4) Hornback, J. M.; Proehl, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 7367 and references cited therein.

(5) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500.

0022-3263/81/1946-1965$01.25/0