shift reagent were obtained in a similar manner. However, the chemical shift values reported for these methyl protons in the presence of various azo compounds represent the values where the molar ratio $Eu(fod)_3$/substrate is equal to 0.10.

Acknowledgment. Financial support from the National Science Foundation (Grant No. GP12325) is gratefully acknowledged. We also thank Dr. D. Pucci for providing some europium shift data and Professor S. N. Ege for helpful discussion.

Registry No. 1, 29852-58-2; 2, 40236-56-4; 3, 29852-56-0; 4, 75521-00-5; 5, 40236-61-1; 8b, 75476-38-9; 9, 24652-80-0; 10, 24652-79-7; 11, 59013-79-5; 12, 59013-78-4; 13, 75521-62-9; 14, 75521-63-0.

Syntheses and Reactions of 3-Phenyloxete and the Parent Unsubstituted Oxete

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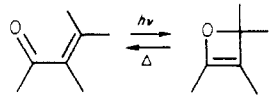
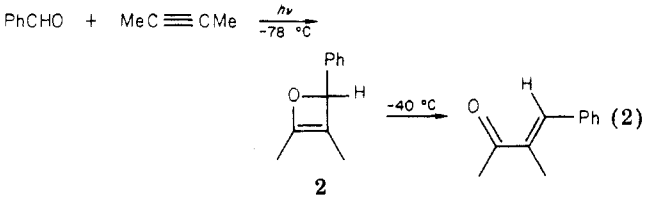
The elimination of *p*-toluenesulfonic acid and *o*-nitrophenylselenilic acid from substituted oxetanes gives 3-phenyloxete (**6**) and oxete (**9**), respectively. 3-Phenyloxete (**6**) undergoes the expected chemistry as well as a facile addition of triplet oxygen to give phenacyl formate (**10**). The parent oxete (**9**) has a thermal half-life in solution at room temperature of ~8 h.

Oxetes have been postulated as reactive intermediates in many types of reactions in the literature.[1] In most cases, the oxetes were unstable toward fragmentation to enones. Even though fluorinated[2] oxetes are quite stable, unfluorinated oxetes have only limited thermal stability. In two cases, we were able to prepare unfluorinated oxetes using photochemical reactions.[3,4] Unfortunately, oxete **1** (eq 1) has a half-life at room temperature of less than a day in most solvents[5] whereas oxete **2** (eq 2) begins to fragment at ~−40 °C.[4]



(1)

1



(2)

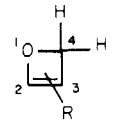
2

Our goal is to prepare oxetes that have greater stability at room temperature so that their chemistry can be studied. One possible application of oxetes in which we are interested is to use them as routes to generate the 6π- and 4π-electron systems **3** and **4**. We have done ab initio

3 **4**

calculations on **3** and **4** which show that these ions should have greatly different energies than their classical models.[6]

In order to prepare more stable oxetes, we felt that an unsubstituted C-4 system was desirable (structure I). The



I

fragmentation mechanism of oxetes to enones appears to be a concerted pericyclic reaction analogous to the fragmentation of cyclobutenes to butadienes.[5] In analogy to cyclobutene substituent effects,[7] most any substituent at C-4 in oxetes would stabilize the transition state for fragmentation. An unsubstituted oxete at C-4, therefore, might be more stable than oxetes **1** and **2**. Also, a C-4-unsubstituted oxete would seemingly be ideal for a possible direct generation of the anion **3** or for free-radical substitution of a C-4 hydrogen with a halogen atom. The 4-halooxetes could then be used for the generation of either anion **3** or cation **4**.

In order to prepare new oxetes, one cannot use the two existing photochemical routes. Each route suffers in not being very general with a wide range of substituents.[8,9] We

(1) (a) See articles cited in ref 4 for photochemical generation of oxetes by [2 + 2] cycloaddition. (b) Vieregge, H.; Schmidt, H. M.; Renema, J.; Bos, H. J. T.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 929. (c) Fuks, R.; Buijle, R.; Viehe, H. G. *Angew. Chem.* **1966**, *5*, 585. (d) Viehe, H. G. *Ibid.* **1967**, *6*, 767. (e) Ficini, J.; Krief, A. *Tetrahedron Lett.* **1967**, 2497. (f) Chapman, O. L.; Adams, W. R. *J. Am. Chem. Soc.* **1967**, *89*, 4243. (g) Chapman, O. L.; Adams, W. R. *Ibid.* **1968**, *90*, 2333. (h) Ficini, J.; Krief, A. *Tetrahedron Lett.* **1969**, 1472. (i) Fuks, R.; Viehe, H. G. *Chem. Ber.* **1970**, *103*, 564. (j) Neuenschwander, M.; Wiedmer, E.; Niederhauser, A. *Chimia* **1971**, *25*, 334. (k) Moriconi, E. J.; Shimakawa, Y. *J. Org. Chem.* **1972**, *37*, 196. (l) Neuenschwander, M.; Niederhaser, A. *Chimia* **1973**, *27*, 379. (m) Ficini, J.; Genêt, J.-P.; Depezay, J.-C. *Bull. Soc. Chim. Fr.* **1973**, *40*, 3367, 3369. (n) Musterd, A.; Matser, H. J.; Bos, H. J. T. *Tetrahedron Lett.* **1974**, 4179. (o) Lahiri, S.; Dabral, V.; George, M. V. *Ibid.* **1976**, 2259. (p) Hartmann, A. G.; Bhattacharjya, A. *J. Am. Chem. Soc.* **1976**, *98*, 7081. (q) Goldfarb, T. D. *J. Photochem.* **1978**, *8*, 29.

(2) (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1307. (b) Hollander, J.; Woolf, C. (Allied Chemical Corp.) Belgian Patent 671 439, 1966; *Chem. Abst.* **1966**, *65*, 8875*b*. (c) Kobayashi, Y.; Hanzawa, Y.; Migashita, W.; Kashiwagi, T.; Nakano, T.; Kumadaki, I. *J. Am. Chem. Soc.* **1979**, *101*, 6445.

(3) Friedrich, L. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1969**, *91*, 7204.

(4) Friedrich, L. E.; Bower, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 6869.

(5) Friedrich, L. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1971**, *93*, 4602.

(6) Friedrich, L. E.; Lam, P. Y.-S. *Tetrahedron Lett.* **1980**, 1807.

(7) Frey, H. M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1169.

(8) Unpublished results of L. E. Friedrich and G. B. Schuster, Department of Chemistry, University of Rochester, 1972.

(9) Unpublished results of L. E. Friedrich and J. B. Bower, Department of Chemistry, University of Rochester, 1974.

0022-3263/81/1946-0306$01.00/0

therefore have concentrated on new thermal routes.

Accordingly, our initial target was to find a way to eliminate *p*-toluenesulfonic acid (pTSA) from tosylate **5c**. The phenyl group was incorporated into the system for the purpose of decreasing the volatility of the oxete and perhaps stabilizing the ring by conjugation. During the course of the work with 3-phenyloxete, an unusually facile addition of oxygen to the oxete was discovered and is described. Last, a synthesis of the parent oxete is given which now makes this system available for future study.

Results and Discussion

A. Synthesis of 3-Phenyloxete (6). The starting point was the available alcohol **5a**, prepared by photolysis of α-methoxyacetophenone (eq 3).[10] The *p*-toluenesulfinic

(3)

5a, X = OH
b, X = OS(O)Tol
c, X = OTs

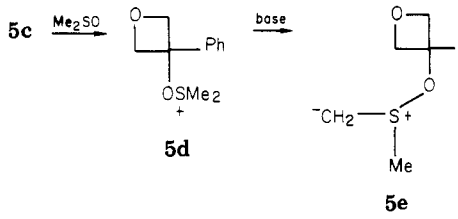
6

acid ester **5b** was prepared, followed by Coates'[11] peracid oxidation method, to give tosylate **5c**. As expected, the tertiary benzylic tosylate was very unstable and decomposed even as a crystalline solid at room temperature within 1 day.

A variety of methods were investigated to effect elimination of pTSA from tosylate **5c**. For our purposes, the best was to dissolve the tosylate in hexamethylphosphoramide (HMPA) followed by the addition of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) under N_2. Workup and low-temperature recrystallization under N_2 gave a product that reacted rapidly with air as well as slowly rearranged to an unsaturated aldehyde (see below).

In the ^1H NMR, the vinyl hydrogen absorbed under the phenyl multiplet and cannot be "seen". The presence of the vinyl hydrogen was indirectly established by ^{13}C NMR. In HMPA, the C-2 vinyl carbon of oxete **6** absorbed at δ 152 as a doublet (J = 193 Hz) due to coupling with the vinyl hydrogen. The C-4 methylene carbon was a triplet (J = 157 Hz) at 81 ppm (see Experimental Section).

In another series of experiments for generation of oxete **6** from tosylate **5c**, the tosylate was dissolved in dimethyl sulfoxide (Me_2SO) under N_2. Within 10 min, the original spectrum of tosylate **5c** changed to that of the alkoxy sulfonium salt **5d** (eq 4). The methylene signal was a

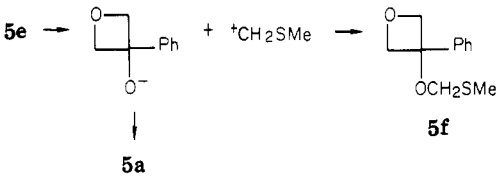


(4)

5d **5e**

singlet at δ 5.07 (4 H), which might suggest a rapidly exchanging sulfonium salt **5d** in which Me_2SO solvation occurs from both faces of the oxetane ring. Such a case is unlikely because such exchange would also signal average the methyl sulfonium singlet at δ 3.13 (6 H) and those of bulk Me_2SO at δ 2.62. The possibility of a symmetrically solvated carbonium ion by Me_2SO is also ruled out because the methyl sulfonium hydrogens at δ 3.13 only integrated to 6 H. Probably, the δ 5.07 singlet is due to an accidental degeneracy as is observed for alcohol **5a** in $CDCl_3$.

We had hoped that treatment of **5d** with a base would generate the sulfur ylide **5e** followed by a syn elimination of Me_2SO to give oxete **6**. Unfortunately, the use of a variety of bases, including the hindered diisopropylethylamine,[12] gave poorer yields of oxete **6** than when no bases were used at all. When bases are used in Me_2SO, the major identified products are believed to be the methyl thioacetal **5f** (eq 5), derived from a Pummerer-type rearrangement,[12] and alcohol **5a** in a 1:3 ratio.



(5)

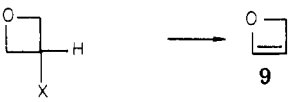
One other elimination method of special interest was the treatment of alcohol **5a** with sulfurane **7** (R_F = $PhC(CF_3)_2$) (eq 6). Martin has shown this to be a mild way to de-

$$\mathbf{5a} + \underset{\mathbf{7}}{Ph_2S(OR_F)_2} \rightarrow \mathbf{6} + Ph_2SO + R_FOH \qquad (6)$$

hydrate tertiary alcohols.[13] We did not pursue this reaction very far because we thought there would be great difficulty in separating the reaction byproduct from the unstable oxete **6**. From our limited experience, however, the use of sulfurane **7** gave a quantitative yield of oxete **6** based on ^1H NMR analysis and could prove to be a useful reagent for other difficult dehydrations.

Other methods were investigated to prepare oxete **6** from the alcohol **5a** and its derivatives. Some of these are summarized in the Experimental Section. None of these reactions were extensively optimized because the HMPA/DBU route appeared to have the greatest promise.

B. Synthesis of the Parent Oxete. For the synthesis of the parent oxete our starting material was 3-oxetanol (**8a**, eq 7),[14] made ultimately from allyl alcohol. Since Wojtowicz[14] was unsuccessful at preparing oxete from the tosylate of alcohol **8a**, we decided to pursue a different route.



(7)

8a, X = OH
b, X = *o*-NO_2PhSe
c, X = *o*-NO_2PhSeO

9

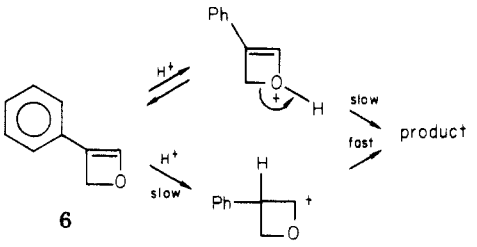
The method we used was that in which alcohol **8a** was allowed to react with tri-*n*-butylphosphine and *o*-nitrophenyl selenocyanate[15] to give the selenide **8b**. The oxide **8c** was produced by ozonolysis[16] at low temperature. Warming of the selenoxide in the presence of DBU with nitrogen bubbling gave a low yield of oxete (**9**) contaminated primarily with the solvent triglyme. The ^1H NMR of oxete consists of three peaks whose shifts are shown in comparison with those of *N*-(carbomethoxy)-2-azetine[17]

(10) (a) Yates, P.; Szabo, A. G. *Tetrahedron Lett.* **1968**, *991*. (b) Lewis, F. D.; Turro, N. J. *Mol. Photochem.* **1970**, *92*, 311.
(11) Coates, R. M.; Chen, J. P. *Tetrahedron Lett.* **1969**, 2705.
(12) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.
(13) (a) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 4327; (b) Kaplan, L. J.; Martin, J. C. *Ibid.* **1973**, *95*, 793.
(14) Wojtowicz, J. A.; Polak, R. J. *J. Org. Chem.* **1973**, *38*, 2061.
(15) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.
(16) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(17) Warrener, R. N.; Kretschmer, G. *J. Chem. Soc., Chem. Commun.* **1977**, 806.

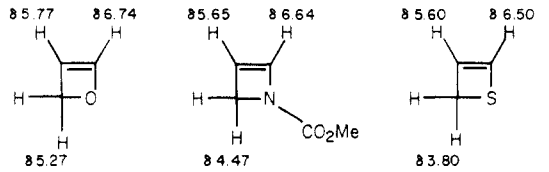
Table I. Approximate Half-Lives of Thermal Ring Opening of Oxetes at 25 °C

oxete	$t_{1/2}$, h	solvent
parent (9)	8.4	$CDCl_3$
3-Ph (6)	14.0	$CDCl_3$
2,3,4,4-Me_4 (1)	16.0	CH_3CN[5]
2,3-Me_2-4-Ph (2)	$\sim 10^{-4}$	$CFCl_3$[4]

Scheme I



and thiete.[18] Our ^1H NMR data (see structures II–IV) are in complete agreement with that reported by Shevlin.[19]



II III IV

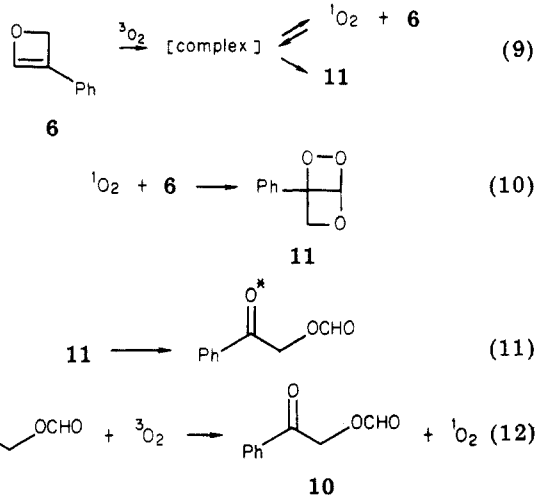
C. Chemistry of 3-Phenyloxete (6) and Oxete (9).

(1) Electrocyclic Ring Opening. The rates of the thermal ring opening of oxetes **6** and **9** were measured in $CDCl_3$ by ^1H NMR. Neither oxete was pure due to difficulty in purification, and therefore all the rate constants are expressed as approximate half-lives. The half-lives of oxetes **6** and **9** as well as other oxetes are shown in Table I. In all cases, the products are the respective unsaturated ketones or aldehydes.

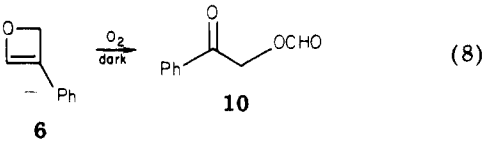
The set of substituent effects on oxete and cyclobutene ring openings is similar. In cyclobutenes, methyl substituents on the double bond slightly raise $\Delta G^{\ddagger}$[7] whereas C-3 methyl groups slightly lower $\Delta G^{\ddagger}$.[7] In 2,3,4,4-tetramethyloxete (**1**), these effects appear to approximately cancel and produce a stability that is similar to that of the parent oxete (**9**). Phenyl substituents on cyclobutene double bonds hardly effect $\Delta G^{\ddagger}$,[20] whereas 3-phenylcyclobutene has a $\Delta G^{\ddagger}$ which is more than 5 kcal/mol lower than unsubstituted cyclobutene (extrapolated to 25 °C).[20] Similar effects of a phenyl substituent are seen on the ring-openings of oxetes **6** and 2,3-dimethyl-4-phenyloxete (**2**).

(2) Acid-Catalyzed Ring Opening. The ring openings of oxetes **1** and **2** were previously shown to be strongly acid catalyzed.[4,5] One drop of acid causes an instantaneous disappearance of the oxetes. The same is true for the parent oxete (**9**). Addition of 0.2 M trifluoroacetic acid in $CDCl_3$ causes oxete (**9**) to disappear within 10 min. On the other hand, the phenyl oxete **6** was stable for over 1 h with 0.15 M trifluoroacetic acid. The reason for the special stability of the 3-phenyloxete to acid must be related to the resonance of the phenyl group with the enol ether. Such stabilizing resonance would retard the rate-determining steps of the two reasonable mechanisms for fragmentation (Scheme I).

Scheme II. Possible $^1O_2$ Pathway for Air Oxidation of Oxete 6



(3) Air Oxidation of Oxete 6. The benefit of the phenyl group in stabilizing oxete **6** to acid was nullified by the activation it provided toward reaction with oxygen in the dark. In fact, all manipulations of oxete **6** must be done under N_2, including workups. The product of the air oxidation is phenacyl formate **10** (eq 8) as shown by spectroscopy, combustion analysis, and synthesis.[21] Oxete **6** is the only oxete we have handled that shows this extraordinary reactivity with O_2 in the dark.



Literature autooxidations of π systems typically proceed either by ionic mechanisms[22] that usually involve $^1O_2$ or by radical processes.[22a,23] In the typical $^1O_2$ pathway, the olefin serves to catalyze the $^3O_2$ to $^1O_2$ conversion[22d] (see Scheme II). Reactions 10–12 of Scheme II are the likely propagation steps for product formation. One critical assumption of Scheme II is that dioxetane **11** would fragment to generate the excited state of the product, as do other dioxetanes.[24] Energy transfer from the triplet acetophenone-like excited state to $^3O_2$[25] would generate $^1O_2$ which could continue the chain.

We do not feel that this mechanism is correct for several reasons. First, tetramethylethylene (TME) is an efficient quencher of $^1O_2$ to give tetramethylethylene hydroperoxide (**12**).[26] However, when the autooxidation was conducted in the presence of TME, neither the yield of formate **10**

(18) Dittmer, D. C.; Chang, P. L.-F.; Davis, F. A.; Iwanami, M.; Stamos, I. K.; Takahashi, K. *J. Org. Chem.* **1972**, *37*, 1111.

(19) We thank Professor Shevlin for informing us of his results prior to publication. See: Shevlin, P. B.; Martino, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5429.

(20) $\Delta G^{\ddagger}$ at 25 °C calculated from data in: Pomerantz, M.; Hartman, P. H. *Tetrahedron Lett.* **1968**, 991.

(21) Pasto, D. J.; Garves, K.; Serve, M. P. *J. Org. Chem.* **1967**, *32*, 774.

(22) (a) Turro, N. J.; Chow, M.-F.; Ito, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5580. (b) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 519. (c) Toda, F.; Dan, N.; Tanaka, K.; Takehira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 4529. (d) Turro, N. J.; Ramamurthy, V.; Liu, K.-C.; Krebs, A.; Kemper, R. *Ibid.* **1976**, *98*, 6758 and references cited therein.

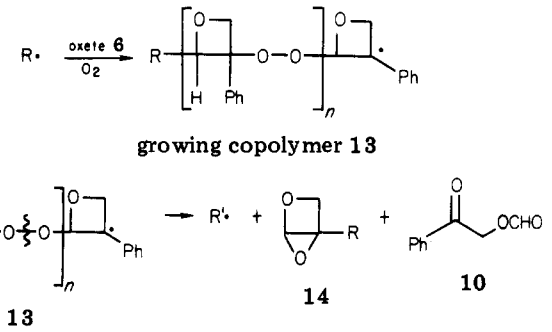
(23) (a) Jefford, C. W.; Boschung, A. F.; Rimbault, C. G. *Helv. Chim. Acta* **1976**, *59*, 2542. (b) Miller, A. A.; Mayo, F. R. *J. Am. Chem. Soc.* **1956**, *78*, 1017. (c) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193. (d) Mayo, F. R.; Miller, A. A. *J. Am. Chem. Soc.* **1958**, *80*, 2480.

(24) Turro, N. J.; Lechtken, P.; Shore, N. E.; Schuster, G.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97.

(25) Shimiza, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.

(26) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741.

Scheme III. Possible Radical Pathway for the Air Oxidation of Oxete 6



nor the rate of disappearance of oxete **6** was appreciably affected. Also, no hydroperoxide **12** was formed. A control experiment showed that **12** is formed in the presence of oxete **6** when $^1O_2$ is generated by dye sensitization.[27]

Second, a free-radical quencher, di-*tert*-butyl-*p*-cresol (DBPC),[28] does inhibit the oxidation more than it quenches $^1O_2$. In benzene-d_6 solvent, 0.026 M DBPC has a $k_q\tau Q$ for quenching $^1O_2$ of $(0.64 \times 10^6)^{29} \times (36 \times 10^{-6})^{30} \times 0.026 = 0.60$. That is, a maximum of ~40% of any $^1O_2$ present could have been quenched by DBPC, whereas the disappearance of oxete **6** was quenched by ~80%.

Third, the yield of formate **10** is undiminished when the oxygenation is done in MeOH solvent. In some other systems,[22a,31] MeOH sometimes traps intermediates along the pathway from oxete **6** to dioxetane **11**. Such quenching does not always occur, however.[32]

The only result in favor of a $^1O_2$ pathway is the finding that 1,4-diazabicyclo[2.2.2]octane (Dabco) also quenches the oxidation. Dabco is known to efficiently quench $^1O_2$[33] as well as electronically excited states.[34] We do not know the mechanism of the Dabco quenching, but we suspect that it quenches a radical process (see below).

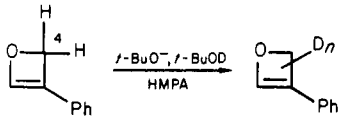
Scheme III shows a possible radical process patterned after the autooxidation of styrene[23b,c] and α-methylstyrene.[23d] The formation of epoxide **14** (which may not be stable) is accompanied by the generation of an alkoxyl radical that depolymerizes with the formation of phenacyl formate. At some point in the depolymerization, the terminal radical, $R^1\cdot$, again begins to copolymerize with oxete **6** and O_2. In the case of neat α-methylstyrene at 50 °C with 154 mm of oxygen pressure (~1 atm of air), the yield of acetophenone (and formaldehyde) is a surprising 67% with an acetophenone–epoxide ratio of 7.3.[23d] The remainder of consumed α-methylstyrene forms a copolymer with oxygen (24%).

The major support for a radical process such as shown in Scheme III is that a free radical quencher, DBPC, inhibits the oxidation. Furthermore, oxete **6** is a substituted styrene and might be expected to autooxidize by a similar mechanism. The major experimental difference between the autooxidations of α-methylstyrene and oxete **6** is that oxete **6** oxidizes much more rapidly. In terms of the mechanism of Scheme III, this could be due to either a more facile production of initiating radicals, R·, that enter propagation, to a longer chain length for propagation, or both.

(4) Other Reactions of Oxete 6. With oxetes **1** and **2**, the ring-opening reactions were so catalyzed by electrophiles that bromination of the double bond was unsuccessful.[4] Oxete **6**, on the other hand, is much less sensitive to electrophiles and does successfully brominate at −15 °C in ether. The stereochemistry of bromination is unknown, and the dibromide, as expected, is rather unstable (see Experimental Section).

Oxete **6** could be hydrogenated to the known[35] 3-phenyloxetane. This result was expected since oxete **1** hydrogenated without difficulty.[3]

Last, an attempt was made to look for exchange of the C-4 hydrogens of oxete **6**. The results of an ab initio



6 ?

calculation[6] on the acidity of the parent oxete suggest that the pK_a of oxetes will be very high and that base-catalyzed hydrogen exchange will be difficult. The conditions chosen were *t*-BuO⁻ in HMPA/*t*-BuOD. The reaction was allowed to proceed until ~20% of oxete **6** remained undecomposed. The remaining oxete was oxygenated to give phenacyl formate **10** which was analyzed by ^1H NMR and mass spectroscopy. No deuterium incorporation was found which suggests that oxete **6** has either a high pK_a and/or the anion reacts before protonation. Similar results have been reported for thiete.[36]

Experimental Section

General Methods. The instruments used were as follows: melting point, calibrated Fisher-Johns; IR, Perkin-Elmer 137 or 467; ^1H NMR, JEOLCO MH-100; FT ^1H NMR and ^{13}C NMR, JEOLCO PFT-100; mass spectroscopy, Du Pont 21-490B; UV, Cary 118C.

3-Phenyloxetan-3-ol (5a). Alcohol **5a** was prepared as described by Yates and Szabo[10a] from photolysis of α-methoxyacetophenone: mp 43–44 °C (after distillation and recrystallization) (lit.[10a] mp 55–56 °C); the conversion was 28%; ^1H NMR ($CDCl_3$) δ 7.70–7.24 (m, 5 H), 4.88 (s, 4 H), 3.74 (s, 1 H); ^1H NMR (Me_2SO) δ 7.74–7.28 (m, 5 H), 6.28 (s, 1 H), 4.81 (d, J = 6 Hz, 2 H), 4.70 (d, J = 6 Hz, 2 H).

3-(*p*-Toluenesulfino)-3-phenyloxetane (5b). In a modification of the general procedure of Wilt, Stein, and Wagner,[37] 2.93 g (16.8 mmol) of *p*-toluenesulfinyl chloride in 25 mL of CH_2Cl_2 was added dropwise to a mixture of 2.50 g (16.7 mmol) of oxetanol **5a**, 1.35 mL (16.7 mmol) of pyridine, and 6 mL of CH_2Cl_2 under N_2 at 0 °C with stirring. An additional 60 mL of CH_2Cl_2 was added, and the mixture was held at 0 °C for 2 h. The CH_2Cl_2 solution was washed with 2 M HCl, 5% $NaHCO_3$, and H_2O and dried over Na_2SO_4. The solvent was evaporated to give 3.96 g (82%) of a colorless oil which was recrystallized from CH_2Cl_2/petroleum ether: mp 70–72 °C (lit.[38] 71.5–72 °C); IR (KBr) 3070,

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1130, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69–7.31 (m, 9 H), 5.41–4.94 (m, 6 peaks, 4 H), 2.43 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.8, 139.1, 129.7, 129.3, 128.9, 127.2, 126.4, 124.7, 83.5, 82.8, 81.2, 21.4.

3-[(*p*-Toluenesulfonyl)oxy]-3-phenyloxetane (5c). By use of the general procedure of Coates and Chen,[11] a solution of 6.68 g (32.9 mmol) of 85% *m*-chloroperbenzoic acid in 115 mL of CH_2Cl_2 was added to a solution of 6.71 g (23.3 mmol) of sulfinate **5b** in 90 mL of CH_2Cl_2 at 0 °C under N_2 with stirring. After 2 h, the mixture was filtered, and the solution was washed twice with 5% K_2CO_3 and H_2O and dried over Na_2SO_4. The solvent was evaporated, and the white solid was tritriated with cold ether/pentane (3:1) to give 7.36 g (100%) of tosylate **5c**. Fast recrystallization from ether gave white needles: mp 71.5–72 °C dec; IR (KBr) 3070, 1340, 1180, 988 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.10 (m, 9 H), 5.30 (d, J = 8 Hz, 2 H), 5.00 (d, J = 8 Hz, 2 H), 2.35 (s, 3 H); ^{13}C NMR (HMPA) δ 144.4 (s), 137.2 (s), 135.7 (s), 130.1 (d), 129.2 (d), 128.7 (d), 127.32 (d), 127.26 (d) 86.21 (s), 81.0 (t, J = 156 Hz), 21.2 (q, J = 131 Hz). The tosylate could be stored only at −20 °C in a freezer.

3-Phenyloxete (6). All liquid compounds were deoxygenated with bubbling N_2 for 15 min. Also, all operations including workup were done under N_2. A 0.31-mL portion (2.0 mmol) of dried 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) was added to a stirred solution of 155 mg (0.51 mmol) of tosylate **5c** in 1.2 mL of dried hexamethylphosphoramide (HMPA; **Caution**! Use a hood.) After 9 h at 25 °C, the solution was added to 50 mL of water (deoxygenated), and the mixture was extracted four times with ether. The combined ether extractions were washed with water and saturated NaCl, and the solvent was removed under vacuum. The crude solid weighed 72 mg and by ^1H NMR contained 10% of tosylate **5c** and 60% of oxete **6** (64% conversion). Most of the tosylate could be removed by precipitation in a small amount of CCl_4. Low-temperature recrystallization of the crude oxete at −78 °C from ether also gives a purer oxete. Flash chromatography[39] on silica gel led to decomposition of the oxete. We have never had oxete **6** completely pure because of decomposition and air oxidation: IR (CCl_4) 3070, 3010, 1630, 982, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.00 (m, 6 H), 5.50 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 149.3 (d, vinyl CH), 129.3, 128.5, 126.1, 122.9, 80.4 (t); ^{13}C NMR (HMPA) δ 152.2 (d, J = 193 Hz), 132.0, 128.5, 125.7, 123.3, 80.6 (t, J = 157 Hz). Impurities made it impossible to definitely assign one sp^2 carbon resonance.

When oxete **6** was added to 0.16 M trifluoroacetic acid in CCl_4, less than 10% decomposition occurred within 1 h.

When DBU was omitted, oxete **6** was formed at a slower rate and in lower yield. After 25 h, ~20% of tosylate **5c** remained, with the formation of ~40% of oxete **6** and 26% of 2-phenylpropenal.

Elimination of Tosylate 5c in Me_2SO. Under N_2, 40 mg (0.13 mmol) of tosylate **5c** was dissolved in 0.3 mL of dried Me_2SO in an NMR tube. The spectrum changed rapidly (5 min) from that of the tosylate [δ 7.29 (br s, 9 H), 5.14 (d, J = 8 Hz, 2 H), 4.92 (d, J = 8 Hz, 2 H), 2.24 (s, 3 H)] to that of sulfonium salt **5d**: δ 7.55 (s, 5 H), 7.49 (d, J = 8 Hz, 2 H), 7.12 (d, J = 8 Hz, 2 H), 5.07 (s, 4 H), 3.13 (s, 6 H), 2.34 (s, 3 H). If 1.2 mL of $CDCl_3$ was added, the spectrum of tosylate **5c** reappeared. After 12 h NMR showed that approximately one-third of the sulfonium salt **5d** remained and that ~15% oxete **6**, 20% of alcohol **5a**, and 5% of known 2-phenylpropenal (independently made, see below) were produced.

When bases were also present (1–4 equiv of *t*-BuOK, DBU, NaH, *i*-Pr_2EtN, Et_3N), only ~5% of oxete **6** was formed along with 50–70% of oxetanol **5a** and 15–20% of thiomethyl ether **5f**. Ether **5f** possesses NMR signals in the mixture at δ 7.65–7.10 (m, 5 H), 5.03 (d, J = 8 Hz, 2 H), 4.90 (d, J = 8 Hz, 2 H), 4.32 (s, 2 H), and 2.22 (s, 3 H).

Elimination of Alcohol 5a with Diphenylbis[bis(trifluoromethyl)phenylmethoxy]sulfurane. A solution of 173 mg (0.257 mmol) of oxysulfurane[40] in 1 mL of $CDCl_3$ was added dropwise under N_2 into an NMR tube containing 39 mg (0.26 mmol) of oxetanol **5a** and 55 mg (0.51 mmol) of 2,6-lutidine (distilled over $AlCl_3$) in 0.25 mL of $CDCl_3$. After a few minutes, ^1H NMR showed no further reaction and a mixture of 62% oxete **6** and 38% unreacted alcohol **5a** (100% yield).

Other Elimination Methods To Prepare Oxete 6. A variety of other methods were investigated. Among them the use of lithium isopropylcyclohexylamide or DBU in tetrahydrofuran solution to eliminate tosylate **5c** gave 5–30% yields of oxete **6**. The use of just DMF, DBU, or pyridine solvent with no other bases gave 12–40% yields of oxete **6** (DBU was the best.)

Treatment of alcohol **5a** with methanesulfonyl chloride in DMF gave 12% of oxete **6**. The use of Burgess' salt[41] in benzene solution gave 18% of oxete **6**.

2-Phenylpropenal. Following the procedure of Kartashov,[42] 1-phenylprop-2-en-1-ol was treated with *tert*-butyl hypochlorite in CH_2Cl_2. After distillation in the presence of hydroquinone, a 30% conversion of 2-phenylpropenal was formed: bp 75–80 °C (5 mm) [lit.[42] bp 75 °C (5 mm)]; UV (hexane) 255 nm (ϵ 4130); IR (neat) 2810, 2705, 1695, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.60 (s, 1 H), 7.50–7.10 (m, 5 H), 6.42 (s, 1 H), 5.96 (s, 1 H).

3-Oxetanol (8a). Oxetanol was prepared by the method of Wojtowicz:[14] bp 67–70 °C (8 mm) [lit.[14] bp 72–73 °C (9 mm)]; ^1H NMR ($CDCl_3$) δ 4.76–4.50 (m, 4 H), 4.50–4.30 (m, 2 H).

3-Oxetanyl *o*-Nitrophenyl Selenide (8b). All reagents and solvents were dried and deoxygenated by bubbling N_2 through them for 5 min. By use of Grieco's procedure[15] for dodecanol, 73 mg (0.36 mmol) of tri-*n*-butylphosphine was added dropwise to a solution of 82 mg (0.36 mmol) of *o*-nitrophenyl selenocyanate and 24 mg (0.32 mmol) of alcohol **8a** in 0.5 mL of pyridine at 25 °C. The solution turned dark brown. ^1H NMR showed the formation of an intermediate (probably an oxyphosphonium salt) which required heating at 70 °C for 2 h to form selenide **8b**. The solvent was evaporated to give 176 mg of a brown oil which was preparatively chromatographed on silica gel (2 mm thick; hexane–Et_2O, 2:1). Elution (R_f 0.71) gave 29 mg (35%) of a yellow solid, **8b**: mp 85–88 °C; IR (KBr) 1590, 1555, 1505, 1320, 979 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.27 (d, J = 7 Hz, 1 H), 7.50–7.00 (m, 3 H), 5.26 (t, J = 6 Hz, 2 H), 4.80–4.60 (m, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 261–255 (selenium isotope peaks for parent at 259 (15)), 229 (24), 186 (100), 156 (36), 91 (22), 78 (18), 57 (12). If oxygen was present, *o,o'*-dinitrodiphenyl diselenide was obtained: mp 208–209 °C (lit.[43] mp 209 °C); ^1H NMR ($CDCl_3$) δ 8.50–7.36 (m).

Oxete 9. Modifying Reich's[16] procedure, a solution of 300 mg (1.16 mmol) of crude selenide **8b** in 4 mL of dried triglyme was ozonized at −55 °C. TLC showed complete loss of **8b**. After nitrogen bubbling for 5 min, 400 μL (2.68 mmol) of dried DBU was added. The solution was immediately heated at 45 °C for 2 h with vigorous N_2 bubbling. The nitrogen stream was passed through a trap cooled with liquid N_2. ^1H NMR showed oxete (**9**) and about an equal amount of triglyme. Fourier transform ^1H NMR ($CDCl_3$) δ 6.74 (br s, $w_{1/2}$ = 2.8 Hz, 1 H), 5.77 (br s, $w_{1/2}$ = 2.8 Hz, 1 H), 5.27 (unresolved t, $J \approx$ 0.8 Hz, 2 H). The yield was only ~5%.

Heating oxete (**9**) in $CDCl_3$ for 40 min at 55 °C gave acrolein quantitatively: IR ($CDCl_3$) 2780, 2700, 1700, 1210, 1160; ^1H NMR ($CDCl_3$) δ 9.63 (m, 1 H), 6.56–6.32 (m, 3 H).

Addition of trifluoroacetic acid to a $CDCl_3$ solution of the oxete (0.16 M in acid) caused complete disappearance of the oxete in less than 10 min.

Kinetics of Thermal Ring-Opening Reactions of Oxetes 6 and 9. A 0.46 M solution of impure oxete **6** in $CDCl_3$ was monitored by ^1H NMR at 25 °C under N_2. The disappearance of the δ 5.50 signal of oxete **6** and the appearance of the 2-phenylpropenal signal at δ 5.96 were followed, relative to the phenyl region, δ 7.0–7.5, as an internal standard. The reaction was followed for 1 day at which time ~40% of oxete **6** remained and ~50% of enal had formed.

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The data were processed by the first-order kinetics equation by using a nonlinear least-squares approach that accounts for random error in all observables to give $k_{obsd} = (1.37 \pm 0.15) \times 10^{-5}$ s^{-1}.

A similar experiment with a 0.05 M solution of oxete (**9**) in $CDCl_3$ was followed by Fourier transform ^1H NMR for 40 h, at which time only a few percent of oxete remained with a 98% yield of propenal. The calculated k_{obsd} was $(2.28 \pm 0.76) \times 10^{-5}$ s^{-1}.

Air Oxidation of 3-Phenyloxete (6) to Phenacyl Formate (10). In the preparation of oxete **6**, if the workup was performed in air without nitrogen bubbling of solvents, evaporation of the solvent followed by silica gel chromatography (CH_2Cl_2–Et_2O, 10:1) gave a 38% yield of phenacyl formate (**10**). Recrystallization from ether/petroleum ether gave needles: mp 32.0–32.5 °C (lit.[21] mp 39–40 °C); UV (MeOH) 212 nm (ε 2500), 245 (10200), 281 (1900); IR (neat) 1740, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.16 (s, 1 H), 7.88–7.10 (m, 5 H), 5.38 (s, 2 H); ^1H NMR (HMPA) δ 8.64 (s, 1 H), 8.25–7.47 (m, 5 H), 5.76 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 191.1 (m), 160.0 (td, J = 4, 230 Hz), 134.0 (td, J = 8, 162 Hz), 134.0 (t, J = 7 Hz), 128.9 (dd, J = 163, 8 Hz), 127.8 (td, J = 6, 162 Hz), 65.3 (dt, J = 5, 147 Hz). Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91; O, 29.24. Found: C, 65.52; H, 5.07; O, 29.02 (oxygen is by actual analysis, not by difference).

When the oxete **6** was added to either $CDCl_3$ or CD_3OD (~0.25 M) and air was bubbled through the solution, 65–75% yields of phenacyl formate were indicated by ^1H NMR in less than 10 min. The result in $CDCl_3$ was *independent* of whether the aeration was done under room fluorescent light or completely in the dark.

Phenacyl Formate (10).[21] A solution of 0.88 g (4.4 mmol) of α-bromoacetophenone in 20 mL of 95% ethanol was added to 0.25 g (3.63 mmol) of sodium formate in 2 mL of water. After 2 h at reflux, the solution was extracted with two portions of ether, dried over $MgSO_4$, and evaporated to give the crude product. Trituration with cold petroleum ether/ether gave 0.21 g (29%) of needles: mp 30.5–32.0 °C (lit.[21] mp 39–40 °C); identical IR and ^1H NMR spectra with that derived from oxete **6** and air.

Attempted Quenching of Air Oxidation of Oxete 6. In these experiments, various potential quenchers were added to a 0.2 M solution of oxete **6**. Air (saturated with the solvent and any other volatile quenchers) was bubbled through the solution followed by ^1H NMR analysis for the amount of unreacted oxete **6** and phenacyl formate (**10**).

A. TME. With 0.5 equiv (0.1 M) of tetramethylethylene and oxete in C_6D_6 solution, the yield of phenacyl formate was 65% after 12 min. In a crude kinetics experiment, the rate of disappearance of oxete **6** decreased by ~8% (within experimental error of 0%).

In a control experiment in C_6D_6 solution, 2.7 equiv (0.54 M) of TME and 10^{-4} M *meso*-tetraphenylporphine was irradiated for 5 min with a 275-W sunlamp in the presence of 0.2 M oxete and with air bubbling. ^1H NMR analysis showed twice as much tetramethylethylene hydroperoxide (δ 1.21 for 3-(hydroperoxy)-2,3-dimethylbut-1-ene) as phenacyl formate (**10**). The hydroperoxide was independently prepared in a similar reaction without oxete **6**: ^1H NMR[44] (C_6D_6) δ 6.82 (s, 1 H, OH), 4.91 (br s, 1 H), 4.83 (br s, 1 H), 1.70 (s, 3 H), 1.21 (s, 6 H).

B. DBPC. With 0.13 equiv (0.026 M) of di-*tert*-butyl-*p*-cresol (DBPC) and oxete in C_6D_6 solution, the yield of phenacyl formate was 85% at 50% disappearance in oxete. In a crude kinetics experiment, the rate of oxete disappearance decreased by ~70%. When 0.15 M DBPC was used, the rate of oxete disappearance decreased by over 95%.

C. Dabco. When 0.18 equiv (0.036 M) of 1,4-diazabicyclo[2.2.2]octane (Dabco) and oxete in C_6D_6 was oxygenated, the yield of phenacyl formate (**10**) was 78% after 30 min. The rate of oxete disappearance was decreased by ~80%.

Bromination of Oxete 6. A solution of 19 μL (0.33 mmol) of bromine in 0.5 mL of ether was added to 44 mg (0.33 mmol) of oxete **6** in 1.0 mL of ether at −15 °C under N_2. After 15 min, the decolorized solution was washed with 5% $NaHSO_3$ and saturated NaCl and dried over Na_2SO_4. The crude product was quickly chromatographed by silica gel TLC [2 mm thick silica gel; pentane–ether (5:1) with four drops of Et_3N] to give 18 mg (17%) of dibromide: R_f 0.7; IR (CCl_4) 3060, 3030, 980 cm^{-1}; ^1H NMR δ 7.57–7.27 (m, 6 H), 5.91 (dd, J = 7, 0.7 Hz, 1 H), 5.14 (ddd, J = 7, 1.7, 0.7 Hz, 1 H); mass spectrum (70 eV), m/e 184 (19), 182 (19), 104 (34), 103 (100), 77 (43).

Hydrogenation of Oxete 6. A mixture of 15 mg (0.11 mmol) of oxete **6** and 10 mg of 5% Pd/C in 1 mL of ether/pentane (1:1) was stirred over 1 atm of hydrogen at 25 °C. After 5 min, the solution was filtered and chromatographed by TLC (0.5 mm thick silica gel; petroleum ether–ether, 3:1) to give 4 mg (27%) of known[38] 3-phenyloxetane: R_f 0.34; IR (CCl_4) 3060, 3025, 978 cm^{-1}; ^1H NMR δ 7.50–7.25 (m, 5 H), 5.03 (dd, J = 8, 5 Hz, 2 H), 4.77 (t, J = 7 Hz, 2 H), 4.28 (m, 1 H); mass spectrum (70 eV), m/e 105 (35), 104 (70, P − H_2CO), 91 (31), 78 (39), 77 (59), 71 (39), 69 (35), 57 (95), 55 (100).

Attempted Base-Catalyzed Deuterium Exchange of Oxete 6. Approximately 0.6 mmol of oxete **6** in 2.2 mL of HMPA solution was prepared as described before from 0.33 g (1.08 mmol) of tosylate **5c** and 0.61 mL (4.3 mmol) of DBU. A mixture of 242 mg (2.16 mmol) of *t*-BuOK and 0.93 mL (9.7 mmol) of *t*-BuOD (Aldrich) in 1 mL of HMPA was added under N_2. The reaction mixture was stirred and after 8 h, NMR analysis of a small, worked-up aliquot showed 82% loss of oxete **6**. The reaction was worked up in air using D_2O. Preparative TLC (2 mm thick silica gel, CH_2Cl_2) gave 6.8 mg of formate **10**. Fourier transform ^1H NMR showed a ratio of 2.0:1.0 for the signals at δ 5.38 and 8.16. The mass spectrum at 10 eV showed no deuterium incorporation (<7%).

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Registry No. 5a, 699-73-0; **5b**, 75700-20-8; **5c**, 75700-21-9; **5d**, 75700-22-0; **5f**, 75700-23-1; **6**, 75700-24-2; **6** dibromide derivative, 75700-26-4; **8a**, 7748-36-9; **8b**, 75700-25-3; **9**, 287-25-2; **10**, 55153-12-3; *p*-toluenesulfinyl chloride, 10439-23-3; 1-phenylprop-2-en-1-ol, 4393-06-0; 2-phenylpropenal, 4432-63-7; *o*-nitrophenyl selenocyanate, 51694-22-5; *o,o'*-dinitrodiphenyl diselenide, 35350-43-7; acrolein, 107-02-8; α-methylstyrene, 98-83-9; acetophenone, 98-86-2; formaldehyde, 50-00-0; α-methylstyrene oxygen copolymer, 31095-11-1; α-bromoacetophenone, 70-11-1.

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