and purified on a silica gel column chromatography (ethyl acetate:*n*-hexane = 1:4–1:1 v/v) to give 0.24 g (77% yield) of monovalerate **3b**: $[\alpha]^{23}_D$ +3.3° (*c* 1, $CHCl_3$); ^1H NMR δ 0.91 (3 H, t, *J* = 7.2 Hz), 1.34 (2 H, tq, *J* = 7.2, 7.2 Hz), 1.60 (2 H, tt, *J* = 7.2, 7.2 Hz), 2.33 (2 H, t, *J* = 7.2 Hz), 3.65 (2 H, m), 3.94 (1 H, m), 4.23 (2 H, d, *J* = 5.6 Hz), 5.11 (2 H, s), 5.20 (1 H, br), 7.36 (5 H, s). For determination of the optical purity, compound **3b** was converted to the (+)-MTPA ester[10] and analyzed by ^1H NMR in the presence of $Eu(hfc)_3$ to establish an enantiomeric excess greater than 97% (a single peak for OCH_2 at 4.85 ppm). The configuration was determined to be *R* after correlation with authentic (*S*)-**3b** prepared from *N*-(benzyloxycarbonyl)-L-serine methyl ester; thus a complete reversal of enantioselectivity was observed in this case. For preparation of the *S* monovalerate, divalerate **4b** was subjected to hydrolysis[8] catalyzed by the same enzyme to give, as expected, the *S* enantiomer in 55% isolated yield and >97% ee (a single peak for OCH_2 at 4.65 ppm).

With regard to the rate of enzymatic transesterification, the ratio of ethyl acetate:isopropenyl acetate:vinyl acetate:vinyl valerate is about 1:100:400:2000. The enol esters are readily available and easy to manipulate. If necessary, the ester with a long acyl chain can be prepared from a carboxylic acid and propyne catalyzed by $Ru(COD)_2$/PR.[11]

In summary, these *irreversible* enzymatic acylation and hydrolysis processes provide new routes to useful chirons in both enantiomeric forms.[12] Application of this procedure to the resolution of other chiral and prochiral alcohols is in progress.

(9) Of the enol esters tested, vinyl valerate gave the best enantioselectivity and rate.

(10) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(11) Watanabe, Y.; Yamakawa, Y.; Hori, Y.; Mitsudo, T. *J. Org. Chem.* **1987**, *52*, 2230–9.

(12) The compounds prepared are useful chiral building blocks. Compound (*S*)-**3a** is useful for the syntheses of platelet activating factor and other phospholipids (ref 6). Compound (*S*)-**3b** can be used in the synthesis of phospholipase A2 inhibitors (Dennis, E. A. *Bio/Technology* **1987**, *5*, 1294. Chandrakumar, N. S.; Hajdu, J. *J. Org. Chem.* **1983**, *48*, 1197). Currently, compound (*S*)-**5** is prepared from D-mannitol (Hirth, G.; Walther, W. *Helv. Chim. Acta* **1985**, *68*, 1863. Fisher, H. O. L.; Baer, E. *Ibid.* **1934**, *17*, 622); compound (*R*)-**5** is prepared from ascorbic acid (Jung, M. E.; Shaw, *J. Am. Chem. Soc.* **1980**, *102*, 6304. Morgenlie, S. *Carbohydr. Res.* **1982**, *107*, 137), L-serine (Hirth, G. et al. as described above), and others (Wilde, H. D.; Clercg, P. D.; Vandewalle, M.; Roper, H. *Tetrahedron Lett.* **1987**, *28*, 4757–8 and references cited therein).

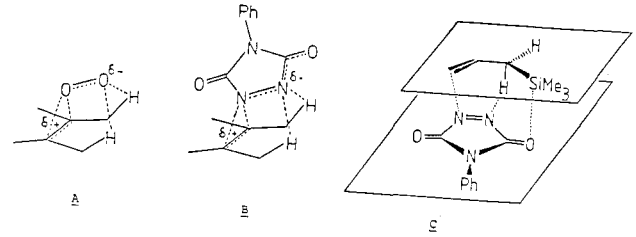
Yi-Fong Wang, Chi-Huey Wong*
Department of Chemistry
Texas A&M University
College Station, Texas 77843
Received February 2, 1988

How Mechanistically Equivalent Are Singlet Oxygen and Triazolinedione? Regiochemical and Stereochemical Differences in Their Ene Reactions with Allylsilanes†

Summary: The usual syn regioselectivity of $^1O_2$ is observed and the gem regioselectivity of PTAD is also observed for these enophiles with allylsilanes, but while $^1O_2$ leads to trans product, PTAD affords cis product; coordination of the silyl groups with these enophiles is thought to be responsible for this mechanistic dichotomy.

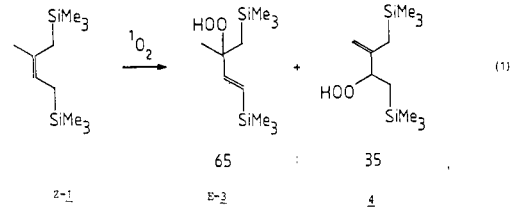
†Dedicated to Prof. F. D. Greene on the occasion of his 60th birthday for his pioneering contributions in this area.

Sir: Presently we report preliminary stereochemical results for the ene reactions of (*E*)- and (*Z*)-1,4-bis(trimethylsilyl)-2-methylbut-2-ene (**1**) with $^1O_2$ and PTAD, which suggest that the mechanistic equivalence of these two enophiles, i.e. the perepoxide-type (A) and the aziridinium



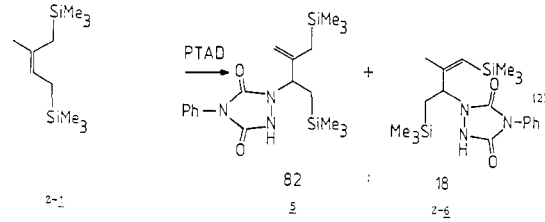
imide type (B) activated complexes, respectively, is not as general as previously implied.[1] As for the alkene diastereomers (*E*/*Z*)-**2**, with $^1O_2$ syn selectivity[2,3] and with PTAD gem selectivity[1,4] is exercised, of course the trimethylsilyl groups causing substantial changes in the regioisomeric composition.[5] More significantly, while $^1O_2$ affords the *E* product for both substrates **1** and **2**, PTAD leads to the *Z* product with the disilylated alkene **1**, but the *E* product with the alkene **2** (cf. regioisomeric and diastereoisomeric fingerprints in Scheme I).

Tetraphenylporphine (TPP) sensitized photooxygenation of the pure (*Z*)-**1** diastereomer in CCl_4 at 0 °C led to the regioisomers **3** and **4** in 65:35 relative proportion (eq 1), as calculated from the 200-MHz ^1H NMR



spectrum of the crude photooxygenation mixture. The trans stereochemistry in (*E*)-**3** was evident from the AB pattern of the olefinic protons at 5.87 ppm with a large coupling of J_{AB} = 19.1 Hz, while cis-configurated vinylsilanes typically show a coupling of ca. 15 Hz.[5a,b] No significant quantities of the cis stereoisomer could be detected by ^1H and ^{13}C NMR.

In contrast to $^1O_2$, the ene reaction of pure (*Z*)-**1** with PTAD in CH_2Cl_2 at ca. 20 °C gave a 82:18 mixture (by ^1H NMR taken on the crude product mixture) of the two regioisomeric urazoles **5** and **6** (eq 2). The stereochemistry



of the minor regioisomer (*Z*)-**6** was assessed by an X-ray structure determination.[6] The ^1H and ^{13}C NMR spectra

(1) (a) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910. (b) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548.

(2) Orfanopoulos, M. G.; Grdina, M. D.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275.

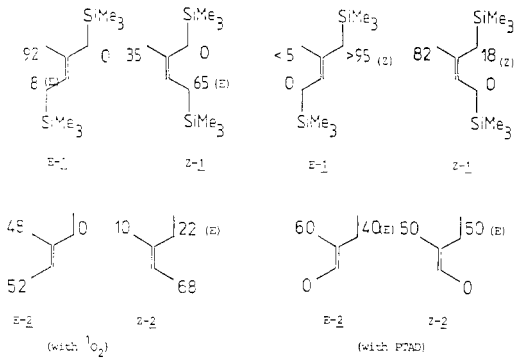
(3) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419.

(4) Griesbeck, A. Dissertation, University of Munich (1984).

(5) (a) Shimizu, N.; Shibata, F.; Imazu, S.; Tsuno, Y. *Chem. Lett.* **1987**, 1071. (b) Dubac, J.; Laporterie, A.; Iloughmane, H.; Pillot, J. P.; Deleris, G., Dunogues, J. *J. Organomet. Chem.* **1985**, *281*, 149. (c) Dubac, J.; Laporterie, A. *Chem. Rev.* **1987**, *87*, 319.

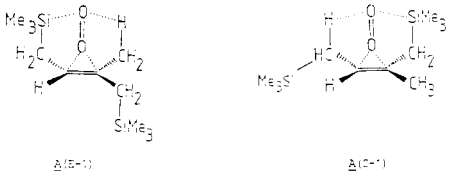
0022-3263/88/1953-3129$01.50/0

Scheme I. Regioisomeric (Numerical Values Represent Relative Percentage Normalized to 100%) and Diastereoisomeric (Configurations Are Given as *E* or *Z* in Parentheses) Fingerprints in the Ene Reactions of O_2 and PTAD with the Disilylated Alkenes (*E*/*Z*)-1 and Alkenes (*E*/*Z*)-2



revealed no detectable amounts of (*E*)-6. Identical products were obtained for the (*E*)-1 diastereomer, i.e., for $^1O_2$ the hydroperoxides (*E*)-3 and 4 and for PTAD the urazoles 5 and (*Z*)-6, but of course with different regioselectivities as shown in the fingerprints of Scheme I. In these experiments no stereochemically pure (*E*)-1 isomer was available, so that a 69:31 mixture of the *E* and *Z* isomers was utilized, but the regioselectivity fingerprints were appropriately corrected.

Besides the pronounced syn selectivity of $^1O_2$, it appears that steric, conformational, and stereoelectronic factors determine the observed regioselectivities in the ene reactions of the disilylated alkenes (*E*/*Z*)-1. Microwave investigations[7a] as well as MM2 calculations[7b] for the parent allylsilane show that the trimethylsilyl group prefers an essentially perpendicular arrangement. This effect is enhanced by severe steric crowding at the geminal methyl site in 1. Therefore, the incoming $^1O_2$ coordinates simultaneously with an allylic hydrogen atom and an allylic silyl group as shown in the transition states A((*E*)-1) and A((*Z*)-1). The activated complex A((*E*)-1) accounts for



the observed syn selectivity as well as for the preferred abstraction from the *gem*-methyl group (92:8 regioselectivity) in (*E*)-1. Furthermore, when the trimethylsilyl group at the less-substituted end accommodates itself within the molecular plane, of course directed away from the *cis*-methyl group, the observed trans configuration in the minor product (*E*)-3 can be reconciled. The activated complex A((*Z*)-1) similarly accounts for the exclusive prototropic shift at the non-geminal trimethylsilyl site and more significantly the trans stereoselectivity in the resulting allylic hydroperoxide (*E*)-3. The appreciable reactivity at the geminal methyl site (35%) is possibly due to steric congestion in the approach of $^1O_2$ from the disilylated side in structure A((*Z*)-1).

An analogous approach of the sterically larger PTAD in transition state B cannot explain the observed gem-type regioselectivity and the cis stereochemistry in the ene products of (*E*/*Z*)-1 (eq 2). Moreover, in the (*E*)-1 diastereomer predominant attack occurs at the *gem*-trimethylsilylmethylene site and in the (*Z*)-1 diastereomer at the *gem*-methyl site, i.e., in both cases the sterically less encumbered hydrogen atoms are preferentially abstracted. This significant result rules out a common intermediate such as a 1,4 dipole as immediate precursor to the ene products of (*E*/*Z*)-1 with PTAD.[8] We propose six-center transition state C with silicon coordination to the carbonyl oxygen. For the (*E*)-1 diastereomer this PTAD approach would explain preferred abstraction at the less hindered geminal site (>95:5 gem selectivity) and cis stereoselectivity in urazole (*Z*)-6 (eq 2). In the case of (*Z*)-1 this type of attack represents the minor pathway (18:82 gem regioselectivity), presumably due to unfavorable steric repulsions between the other trimethylsilyl group and the bulky PTAD moiety at the more crowded disubstituted side.

Dreiding molecular models show that no particular difficulties arise in letting PTAD approach the ene substrate in a parallel plane. In fact, this is essentially the transition state considered previously but discarded on kinetic grounds.[1a] Yet, the consequence of the statement "...resemblance between a carbene and a polarized representation of RTAD..." (ref 1a, p 2915) implies the parallel arrangement between the PTAD enophile and the ene substrate as shown in the transition-state structure C.

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Waldemar Adam,* Michael Schwarm
Institut für Organische Chemie
Universität Würzburg
Am Hubland, 8700 Würzburg, FRG
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