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The Ene Reaction of Allylsilanes with Singlet Oxygen. Unusual Product Stereoselectivity

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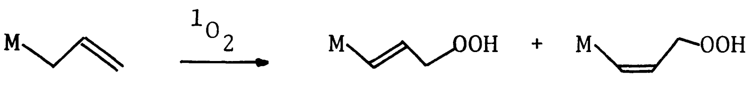
Dye-sensitized photooxidations of allyltrimethylsilanes yield cis ene products predominantly in contrast to the highly stereoselective formation of trans ene products from carbon standards.

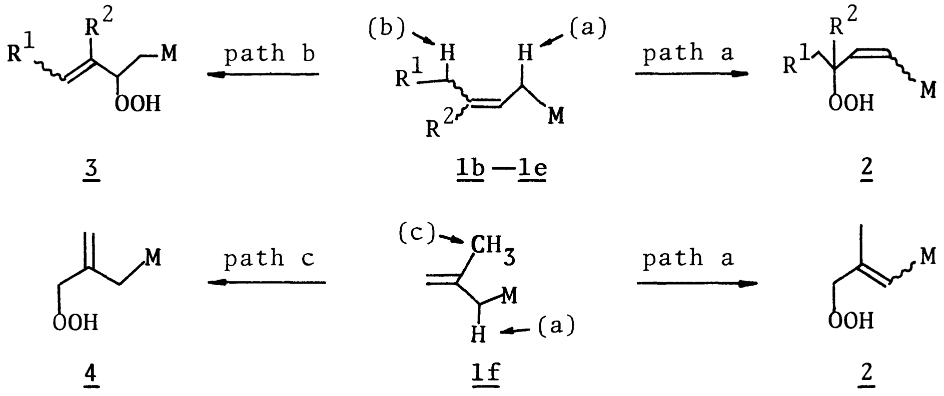
The singlet oxygen ene reaction of acyclic alkenes usually leads to the highly stereoselective formation of allylic hydroperoxides of trans configuration with respect to a newly formed double bond.1) This stereoselectivity, however, has received little attention mechanistically, presumably because of the anticipated stereochemistry on the steric grounds. We report here unusual stereoselectivity of the singlet oxygen ene reaction providing evidence clearly against the steric origin.

Tetraphenylporphyrin-sensitized photooxidations of allyltrimethylsilane (1a) and its 3- or 2-alkyl derivatives 1b—1f in carbon tetrachloride cleanly gave expected ene products (>95% crude yield), 3-trimethylsilylallyl hydroperoxides 2 and their regioisomers 3 or 4, which were isolated as the corresponding alcohols after reduction with sodium borohydride. The structures of the hydroperoxides and the alcohols were confirmed by ^{1}H NMR analysis and the stereochemical assignment was deduced from the coupling constants between the olefinic protons near 14 and 19 Hz for the cis and trans isomers of 2 and the corresponding alcohols. In most cases, the product ratios were determined by NMR analysis of the crude hydroperoxides mixture.2) The results are listed in Table 1 which includes the results with some carbon standards 5—7 for comparison. While neopentylethylene (5) gave a trans hydroperoxide practically in a stereospecific manner, the replacement of an allylic t-butyl group with a structurally related $SiMe_3$ group (TMS) led to not only an increase in reactivity by a factor of 7.1 but also a dramatic change in the stereochemistry of the reaction leading to a predominant (78%) cis selectivity. A low ionization potential of 1a relative to 5 (9.0 and 9.6 eV, respectively3))



	trans-2	cis-2
1a; M=$SiMe_3$	22%	78%
5; M=t-Bu	>99%	<1%

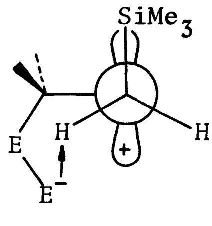
probably accounts for the increased reactivity. trans-2-Pentenyltrimethylsilane (trans-1c) provides an intramolecular example which demonstrates a marked difference between TMS and an alkyl group in the stereochemistry of the singlet oxygen ene reaction; hydrogen abstraction from the ethyl group (path b) gave 3 with a high trans-stereoselectivity (>97%), while that from the trimethylsilylmethyl group (path a) yielded 2 predominantly of cis-configuration (cis/trans=66/34). These



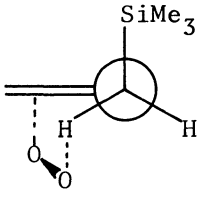
M=SiMe$_3$ or t-Bu

stereochemical findings are hardly rationalized on the steric grounds since TMS itself is a sterically very bulky group as compared to methyl, although TMS might be smaller than t-butyl in its effective size.4) The cis selectivity was markedly dependent on the structure of the allylsilanes as shown in Table 1; the presence of an alkyl group at C$_3$ of the allyl skeleton, especially cis to the CH$_2$TMS group, reduced the cis selectivity.

The unique effect of an allylic TMS would probably be associated with a strong capability of hyperconjugation of a C-Si single bond,5) and two simple models in which hyperconjugation effect operates effectively are a zwitterionic intermediate 8a and a perpendicular conformation 9 (skeletal dihedral angle ∠CCCSi= θ =90°) of an allylsilane. A cis ene product can be formed either from 8a via proton transfer of



8a; E=E: O$_2$
8b; E=E: TCNE



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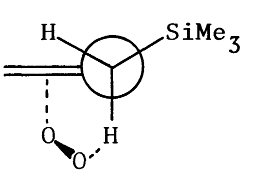

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an inner hydrogen of the CH$_2$TMS group or from 9 via a concerted ene process; since 9 is close to a stable conformation (θ=103°) of allylsilane,6) it would probably be energetically more favorable than an anti form 10 (θ=150°) which leads to a trans ene product. The intervention of 8a, however, is unlikely from the following reasons. First, 8a formed either in a rate-determining step or a product-forming

Table 1. Regio- and stereoselectivities of the singlet oxygen ene reaction of allyltrimethylsilanes[a]

Allyltrimethylsilane (ATMS)	k_{rel}[b]	% path a	% cis of 2
ATMS (1a)	1.0	a only	78
cis-3-Me-ATMS (cis-1b)	31	32, 30[c]	50, 51[c]
trans-3-Me-ATMS (trans-1b)	18	52, 50[c]	66, 69[c]
cis-3-Et-ATMS (cis-1c)	132	40	53
trans-3-Et-ATMS (trans-1c)	33	63	65
cis-3-i-Pr-ATMS (cis-1d)	4.7	>95	12
trans-3-i-Pr-ATMS (trans-1d)	4.7	>95	49
3,3-di-Me-ATMS (1e)	340	33, 29[c]	33, 29[c]
2-Me-ATMS (1f)	12	56	d)
neopentylethylene (5)	0.14	a only	<1
2,5,5-trimethyl-2-hexene (6)		71	<1
2,4,4-trimethyl-1-pentene (7)		<5	

a) In carbon tetrachloride using tetraphenylporphyrin as a sensitizer. b) Determined by a competition experiment technique. c) In acetonitrile using methylene blue as a sensitizer. d) Spectral data suggested that the product was stereochemically a single product.

one is expected to undergo a facile elimination of TMS as a side reaction especially in polar solvents. This process, indeed, is the major course of the reaction between 1a and TCNE, a typical donor-acceptor reaction proceeding via an analogous intermediate 8b, in acetonitrile.[7] In contrast, the photooxidations of all allylsilanes 1a—1f cleanly gave ene products with retention of TMS irrespective of solvent polarity (CCl_4, MeOH, and CH_3CN). Solvent did not play a dominant role in the product regio- and stereoselectivities either. Second, the intervention of a zwitterion should favor the formation of 2 rather than 3 from cis-1b and cis-1c because the cationic center of the intermediate must be more effectively stabilized by a CH_2TMS group than by an alkyl group. This is not the case. Third, the rate-determining formation of 8a suggests a high reactivity of 2-methylallyltrimethylsilane (1f) relative to 1a and a 3-methyl isomer 1b, as was actually observed in the reaction with TCNE (relative reactivity: 1f/trans-1b or 1a > 10^3). In contrast, 1f was in fact less reactive than 1b toward singlet oxygen; the observed reactivity order cis-1b>trans-1b>1f (3:1.6:1) is a typical one for the singlet oxygen ene reaction of disubstituted alkenes.[8] On the other hand, these observations are in accord with the concerted mechanism.[9,10] The observed dependence of the stereoselectivity on the initial geometry of the allylsilanes is also consistent since the perpendicular conformation must be sensitive to the steric effect of an alkyl group at C_3. The stereochemistry itself does not rule out the intervention of a perepoxide intermediate but the regiochemical findings are more in accord with a direct conversion to the product; the product-forming step from the perepoxide would presumably be ionic and favor the formation of 2 rather than 3 in the case of cis 3-alkylallylsilanes 1b and 1c against the observation.[11]

A further systematic study on the stereoselectivity of the ene reactions of allylsilanes with various enophiles is underway.

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2) In most cases, cis-2, trans-2, and 3 (and also the corresponding alcohols) showed the SiMe$_3$ signal near δ =0.14, 0.08, and 0.0, respectively. Typical NMR spectra (400 MHz, CDCl$_3$) are as follows: cis-2c: 0.13 (9H, s), 5.90 (1H, d, J=14.6 Hz), 6.17 (1H, dd, J=14.6 and 9.3 Hz); trans-2c: 0.09 (9H, s), 5.91 (1H, dd, J=18.6 and 5.5 Hz), 5.99 (1H, d, J=18.6 Hz); 3c: 0.01 (9H, s), 5.32 (1H, ddq, J=15.5, 10, and 1.4 Hz), 5.78 (1H, dq, J=15.6 and 6.8 Hz).

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11) In connection with this, a comparison of the regioselectivity of the singlet oxygen ene reaction with that of the ene reaction with 1,2,4-triazolinediones (TAD) which probably proceeds via an aziridinium imide intermediate is informative.[12] Preliminary experiments with 1b and 1c indicated that the reaction was regiospecific to yield ene products of type 2 irrespective of the initial geometry of the starting material, while the reaction with 1e regiospecifically gave an ene product of type 3 consistent with an ionic ring-opening of the intermediate.[13]

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