# *syn*- and *anti*-Sesquinorbornenes as Mechanistic Probes in Reactions of the Carbon–Carbon Double Bond

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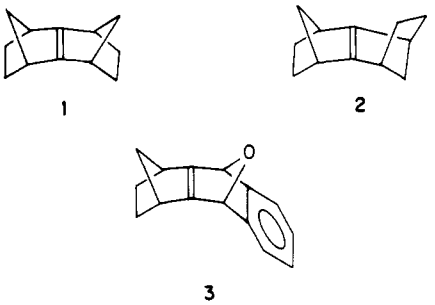
The rates of a number of concerted, free radical, and ionic additions to the double bond of *syn*- and of *anti*-sesquinorbornene have been studied (Table I). Equilibria, where measurable, are more favorable to addition with the anti than with the syn isomer. The rate ratio $k_{syn}/k_{anti}$ varies from less than 0.05 for reversible, ionic additions to 1–7 for free-radical and concerted reactions. A series of substituted phenyl azides reacting with *syn*-sesquinorbornene fit the Hammett equation with $\rho = 1.03$ and a correlation coefficient of 0.995 (omitting the *p*-$NO_2$ substituent, which appears more activating than its normal $\sigma$ constant would indicate). The quantitative results offer insight into some mechanistic details of the reactions with peracids and of photosensitized oxygenations and epoxidations.

## Introduction

The title compounds, **1** and **2**, continue to be of mechanistic interest because some of their special characteristics are useful in sorting out possible reaction mechanisms, especially of addition and elimination reactions. A recent study showed that bromine, acids, alcohols, and water add reversibly to the sesquinorbornenes, the equilibrium in the addition of water or methanol to **2** favoring adduct about



**1** **2** **3**

a thousand times more than in the addition to **1**. Also, the additions of this type to *anti*-sesquinorbornene were much faster than the additions to the syn isomer.[1]

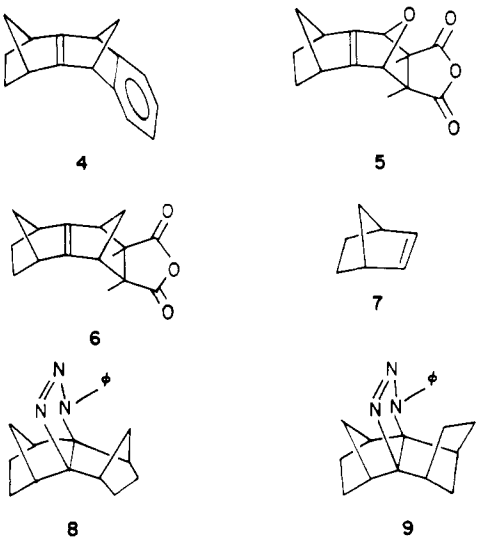
The existence of another class of addition reactions which are irreversible and in which the syn isomer (**1**) is up to seven times more reactive than the anti (**2**) raises the question whether the equilibrium and rate of addition are directly connected to the ionic character of the reactions. In this paper we explore a range of addition reactions to the sesquinorbornenes, observing the competitive behavior of the isomers and seeking correlations between this and the chemical character of the reactions.

A general conclusion from the equilibrium studies was that addition to *syn*-sesquinorbornene, occurring on the less hindered exo face, involves a substantial element of strain from the close approach of the four endo hydrogen atoms on the ethylene bridges, which are forced closer together than their normal van der Waals distance by the saturation of the double bond.

## Results

The experiments listed in Table I were all performed competitively with equivalent amounts of *syn*- and *anti*-sesquinorbornenes reacting with an amount of reagent less than equivalent to one of them. In every case the reaction order was the same for both of the two isomers.

**Concerted Additions.** Phenyl azide presents an example of uncomplicated (2 + 3) cycloaddition to the double bond of sesquinorbornene.[2,3] The syn and anti products, **8** and **9**, are both thermally stable, although these triazo-



**4** **5** **6** **7** **8** **9**

lines can be made to eliminate nitrogen photochemically. The cycloaddition rate ratio, $k_{syn}/k_{anti} = 3.4$, suggests a fairly early transition state since there is no sign of the syn reaction being slowed by the late ethylene bridge compression as in the additions of acids and of bromine to *syn*-sesquinorbornene. It is also clear that the transition state in this addition must be able to approximate the planarity of the triazoline ring in the product, unlike a singlet oxygen transition state (see below), which must comply with special orbital symmetry requirements.

It has been pointed out[4] that the low dipole moment of phenyl azide indicates a large degree of resonance between the possible 1,3-dipolar bond structures of the azide group. This resonance tends to make a symmetrical reagent of the azide, consistent with its functioning as a concerted 1,3-cycloaddition reagent.[5]

Addition of substituted phenyl azides from *p*-methoxy to *p*-nitro, with a range of olefins including norbornene,

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(2) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

(3) Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience Publishers, Wiley: New York, 1964; p 844.

(4) Reference 3, p 835.

(5) The term "concerted" is used here, as in most discussions of reaction mechanisms, to denote a process in which no energy minimum intervenes between reactants and products. There is no implication concerning symmetry of the transition state or synchronism of changes in different parts of the reaction complex.[21]

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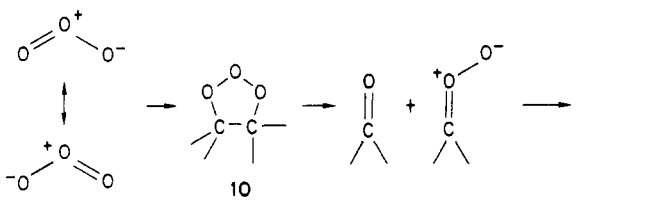
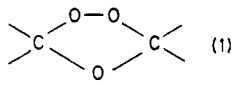
has been reported to follow the Hammett equation closely,[6] with values of $\rho$ from −1.1 for maleic anhydride to +2.54 for 1-pyrrolidinocyclohexene. In our study of substituted phenyl azides added to *syn*-sesquinorbornene (Table III) we observed, as had Scheiner et al.[7] in the case of norbornene, (a) that $\sigma^0$ values based on reaction rates gave appreciably better correlations than $\sigma$ values based on ionization constants and (b) that the *p*-nitro substituent gave consistently higher rates than expected from its $\sigma$ value of 0.78 or its $\sigma^0$ value of 0.73; indeed, from the Hammett $\rho$ of 1.02 derived from seven other substituents, the effective $\sigma^0$ value of *p*-$NO_2$ was calculated to be 1.00, halfway to the special value of $\sigma_{p\text{-}NO_2}$ derived from amines and phenols[8a] (1.27). Smaller, but still abnormally large, $\sigma$ values for *p*-$NO_2$ appeared in our cycloadditions to olefins based on only the *m*-nitro and parent phenyl azides.

In all the reactions listed in Table III the aryl azide has electron acceptor character, and the sesquinorbornenes are appreciably stronger donors than is norbornene.

Benzo-*syn*-oxasesquinorbornene (**3**) is 15.8 times as reactive toward *p*-nitrophenyl azide at 30 °C as is benzo-*syn*-sesquinorbornene (**4**), but this could be the case for steric reasons,[9] in spite of an unfavorable inductive effect of the oxygen bridge cis to the site of the cycloaddition.

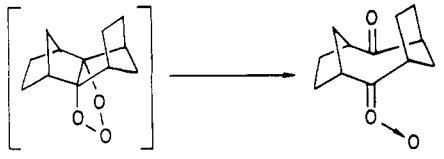
Another concerted reagent in Table I is ozone, representable as a resonance hybrid of the two equivalent 1,3-dipolar structures. Ozone differs from phenyl azide in that in the usual case its direct cycloadduct to the double bond (**10**) undergoes immediate cleavage followed by a new cycloaddition (eq 1). The normal ozonide, the readdition

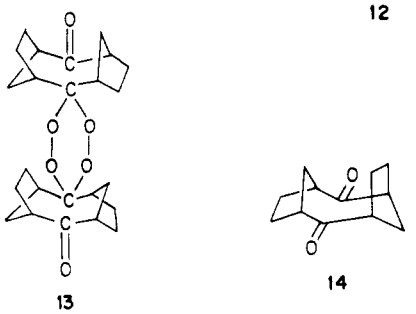



(1)

product **11**, is unknown in the case of sesquinorbornenes, being replaced by the diketo diperoxide **13** from symmetrical dimerization[10] of the carbonyl oxide **12**. This sequence occurs rapidly without evidence of any side reactions of the intermediates. This alteration of the normal ozonization sequence could be considered a predictable consequence of the special stereochemistry of sesquinorbornene: the sterically assisted cleavage of the initial ozonide leads to a keto carbonyl oxide (**12**) which can never assume the distorted conformation required for closure to the pentacyclic version of **11**. At the same time the result shows that in a bimolecular encounter of two molecules of **12**, dimerization of the carbonyl oxide structure is preferred to cross reaction between a CO and a COO group.







In competition of *syn*- and *anti*-sesquinorbornenes for ozone, this reagent appears only about half as selective as is phenyl azide, but it still favors the syn isomer even at the lowest competition temperature of the series (−78 °C).

*Singlet oxygen* is not included in Table I because its extreme unreactivity toward the sesquinorbornenes has made it difficult to study directly or quantitatively. According to the orbital symmetry rules, there are two allowed modes of concerted addition of singlet oxygen to the carbon–carbon double bond, the ($_\pi2_s$ + $_\pi2_a$) addition and the (2 + 1) addition to form a perepoxide. Both of these modes of reaction are severely hindered by the special environment over the double bond of the sesquinorbornenes, and the importance of this effect is emphasized by the great ease with which the related compound, biadamantylidene, forms a stable dioxetane.[11] Recent work, however,[15] has revealed that the complex oxygenation mixtures from various treatments of the sesquinorbornenes do contain small amounts of the diketone which would be a cleavage product of the dioxetane. The formation of even small amounts of ketone opens the way to photosensitized oxidations such as epoxide formation. At least the unique behavior of this olefin–reactant pair is strong evidence that there is no easy stepwise substitute for concerted cycloaddition of molecular oxygen.

A different kind of concerted reaction is cis hydrogenation of the double bond by *diimide*.[13] This is believed to be a concerted donation of two hydrogen atoms by the cis component of the HN=NH generated from azodicarboxylic acid. With SSNB the hydrogen adds only on the exo face; the selectivity ratio is $k_{syn}/k_{anti}$ = 1.2.

The other definitely concerted reagent in Table I is *m-chloroperbenzoic acid* (MCPBA). The evidence for the concerted nature of peracid epoxidation is extensive: in peracid epoxidation configuration is retained, with no inversions such as an open-chained intermediate would permit. (This is in contrast to photosensitized epoxidation involving free radical intermediates and allowing open-chained cis and trans olefins both to form trans epoxide.[16])

This property has led to the suggestion[17] that peracid epoxidation is a concerted donation of O from the cyclic hydrogen-bonded peracid molecule **15**, which in the process

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(8) (a) Hammett, L. P. "Physical Organic Chemistry"; McGraw-Hill: New York, 1940; p 188. (b) Taft, R. W., Jr. *J. Phys. Chem.* **1960**, *64*, 1805.
(9) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.
(10) The formula **13** is not meant to embody any information about composition with respect to the stereoisomeric dimers.
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(17) Bartlett, P. D. *Rec. Chem. Progr.* **1950**, 47–51.

**Table I. Competitive Additions to *syn*- and *anti*-Sesquinorbornenes**

| | reagent | temp, °C | solvent | product | $k_{syn}/k_{anti}$ |
|---|---|---|---|---|---|
| 1 | benzil + $O_2$, light | room temp | benzene | epoxide | 6.7 |
| 2 | acetone (+ free radical initiator) | | | acetonyl adduct | 4.0–4.6 |
| 3 | phenyl azide | 50 | $CH_2Cl_2$ | phenyltriazoline | 3.4 |
| 4 | *m*-chloroperbenzoic acid | 0 | $CH_2Cl_2$ | epoxide | 2.2 |
| 5 | ozone | −78 | pentane | diketodiperoxide | 1.5 |
| 6 | phenyl iododichloride | reflux | $CCl_4$ | dichloride | 1.3 |
| 7 | diimide | room temp | $CH_3OH/CH_2Cl_2$ | $H_2$ adduct | 1.2 |
| 8 | chlorine | room temp | $CH_2Cl_2$ | dichloride | ~1.0 |
| 9 | chlorine, $O_2$ stream | room temp | $CCl_4$ | dichloride | 0.07 |
| 10 | $Br_2$ (dark) | room temp | $CCl_4$ | dibromide | < .05 |
| 11 | hydrogen chloride | 0 | ether | HCl adduct | < .05 |
| 12 | *N*-bromosuccinimide + perchloric acid | room temp | dioxane–$H_2O$ | bromohydrin | < .05 |
| 13 | NBS + light | room temp | dioxane | hydrobromide + dibromide | < .05 |
| 14 | $BrCl_2C-CCl_2Br$ + radical initiator (DBPO) | room temp | $CH_2Cl_2$ | *anti*-dibromide | < .05[a] |
| 15 | hydrogen bromide | 0 | ether | HBr adduct | < .05 |
| 16 | water (acid catalyzed) | 82 | acetonitrile | $H_2O$ adduct | < .05 |

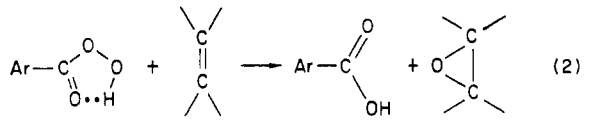
[a] No reaction with *syn*-sesquinorbornene alone.

**Table II. Rate Constants[a,b] for the Reaction of Substituted Phenyl Azides with 2, 3, and 7**

| | olefin | | |
|---|---|---|---|
| X in $XC_6H_4N_3$ | 2 | 3 | 7 |
| H | 1.62 | 2660 | 1.03[c] |
| *p*-$NO_2$ | 14.8 | 16750 | 6.34[c] |
| *m*-$NO_2$ | 7.1 | 8710 | 3.99[c] |
| $k_{p\text{-}NO_2}/k_H$ | 9.14 | 6.30 | 6.16 |
| $k_{m\text{-}NO_2}/k_H$ | 4.38 | 3.21 | 3.87 |
| $(k/k_7)_{p\text{-}NO_2}$ | 2.33 | 26.42 | 1.00 |

[a] $\times 10^{-3}$ L mol$^{-1}$ min$^{-1}$. [b] 30 °C, unless otherwise referred. [c] 25 °C.

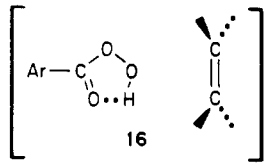
can form a carboxylic acid without any unsaturated intermediates along the way (eq 2).




(2)

15

If the peracid **15** in equation 2 is indeed internally hydrogen bonded, then it performs the epoxidation via a transition state, **16**, where the axis of the C=C double




16

bond is coplanar with the chelated ring of the peracid; no other conformation of the transition state is accessible to either isomer of sesquinorbornene. We may be observing a hard-to-find demonstration that the epoxidation involves a coplanar donation of the oxygen atom with a concerted[5] double inversion, the new bonds of the epoxide being formed in the same plane as the bonds being broken in the chelated peracid. As with the other concerted reactions, the value of $k_{syn}/k_{anti}$, here 2.2, is consistent with an early transition state where the openness of approach to the double bond of **1** outweighs the later mutual hindrance of the ethylene bridges.

We also determined the competitive reaction rates of **1** and **2** toward *benzil-photosensitized epoxidation* in benzene. This proved to be the most syn-selective reaction of all, with $k_{syn}/k_{anti}$ averaging 6.7 in five runs, three times the ratio shown by MCPBA (Table I).

**Radical-Initiated Additions.** One of the clearest *free radical* mechanisms of the sesquinorbornenes is the addition of acetone to yield an H–acetonyl adduct, initiated by di-*tert*-butyl diperoxyoxalate.[14,15] This has been shown to be a chain reaction in which the selectivity is exercised largely by the acetonyl radical adding to one end of the double bond of *syn*- or *anti*-sesquinorbornene. The preference for the syn isomer is larger than that of any concerted reaction in Table I (4–4.6). Again this reaction shows no reversibility. It is not surprising that the addition of a short-lived free radical should have an early transition state and be unaffected by strain arising late in the addition process, but it is of considerable interest that the selectivity is so much closer to those of some concerted additions than to known ionic processes.

## Discussion

Table I may be examined in the light of the earlier observation[1] that one group of reagents shows selectivities $k_{syn}/k_{anti}$ in the range 1–7 while the other reagents have values of this ratio below 0.05. Our previous results fitted the generalization that these low syn/anti ratios were associated with reversible ionic mechanisms, although in every case available at that time the syn adduct could be

**Table III. Reaction Rate of Substituted Phenyl Azides with *syn*-Sesquinorbornene in Ethyl Acetate[a]**

| substituent | $\sigma^{08b}$ | $10^2$[azide]$_0$ | $10^2$[SSNB]$_0$ | adduct × $10^5$, 10 min | $10^3k$ | $k/k_H$ |
|---|---|---|---|---|---|---|
| *p*-MeO | −0.16 | 0.65 | 2.04 | 0.348 | 2.62 | 0.62 |
| *p*-Me | −0.15 | 0.965 | 2.04 | 0.593 | 3.01 | 0.71 |
| H | 0 | 0.83 | 2.04 | 0.7222 | 4.26 | 1.00 |
| *m*-MeO | 0.06 | 0.905 | 2.04 | 0.775 | 4.20 | 0.99 |
| *p*-Br | 0.26 | 0.835 | 0.68 | 0.468 | 8.24 | 1.93 |
| *m*-Br | 0.38 | 0.585 | 2.04 | 1.193 | 10.00 | 2.35 |
| *m*-Br | 0.38 | 0.095 | 2.04 | 0.194 | 10.01 | 2.35 |
| *m*-$NO_2$ | 0.70 | 2.21 | 2.04 | 9.167 | 20.33 | 4.77 |
| *m*-$NO_2$ | 0.70 | 2.21 | 0.68 | 3.190 | 21.23 | 4.98 |
| *p*-$NO_2$ | 0.73 | 0.755 | 2.04 | 6.800 | 44.15 | 10.35 |

[a] $\rho$ = 1.02, $r$ = 0.997 (omitting *p*-$NO_2$).

prepared in good yield in the absence of syn–anti competition.

From this point of view, interest in Table I might center around reactions of chlorine. Ordinary chlorination at room temperature in methylene chloride solvent yields similar amounts of syn and anti dichlorides under competitive conditions, while chlorination in an oxygen stream shows the strong preference for anti which characterizes the ionic reactions. Since chlorine is known[18] to be capable of reaction by a chloronium ion mechanism, this pair of observations can be interpreted in terms of the ionic and free radical mechanisms. Pure chlorine may prefer to react by a radical chain, which, however, is efficiently inhibited by molecular oxygen, opening the way for the second-choice ionic mechanism.

Why should these two stepwise mechanisms differ sharply in their selectivity between ASNB and SSNB? If, as in some well-documented acyclic cases, the chlorocation is a cyclic chloronium ion, all the hindrance to addition to *syn*-sesquinorbornene could be encountered in the first step, in which this cation is formed with $sp^3$ hybridization at both ends of the double bond, whereas the required approach of the bridges trans to the halogen atom in the anti isomer would be relatively favorable. On this view, the difference in syn–anti selectivity between chlorine and bromine means that bromine is strongly predisposed toward bromonium ion formation, and no conditions have been found for making it attack SSNB homolytically.

There is a radical chain reaction by which bromine can be added to *anti*-sesquinorbornene, namely the use of 1,2-dibromotetrachloroethane initiated by di-*tert*-butyl diperoxyoxalate (suggested to us by Professor P. S. Skell). However, this reaction could not be used to determine the stereoselectivity of atomic bromination, since pure *syn*-sesquinorbornene gave no reaction under these conditions. Since addition of elementary bromine to SSNB is detectably reversible, it is not surprising that in the transfer of $Br_2$ between SSNB and tetrachloroethylene the equilibrium lies strongly toward the $BrCCl_2CCl_2Br$.

The most obvious difference between additions to the two SNB isomers is that, unlike the anti system, *syn*-sesquinorbornene on addition yields a product with serious compression between two pairs of endo hydrogens on its ethylene bridges. If the addition is stepwise, this energy barrier is in two parts, and the greater hindrance occurs late in the addition when the rehybridization is complete at both 4a and 8a. Hence any mechanism involving a late transition state will discriminate in favor of ASNB in comparison to a mechanism with an early transition state, where some advantage can be discerned in the approach of a reagent to the syn isomer. It seems likely at present that in most free-radical mechanisms the formation of a new bond to the SNB is rate determining, which causes the transition state to occur in that stage where the syn isomer is favored because of the easy approach to the unsaturated carbon. The same is normally true of concerted reactions, where it is easier to get the addition reaction started in the syn isomer, and the energy relations are such that by the time total symmetrization occurs in the formation of the new bonds, the transition state has been passed.

Reactions proceeding through a cationic intermediate constitute a special case. All our results place these reactions in the class of those with late transition states. This could be because of a rate-determining combination of a stabilized cation with an anion or because the main activation barrier occurs in formation of the cation, after which completion of the reaction is electrostatically downhill. An example of the latter situation would be the bromonium bromide or tribromide of biadamantylidene.[18]

Our SNB dibromides, however, are soluble in nonpolar solvents and do not have the properties of the less strained bromonium salts. It appears that the bridge compression strain in the bromonium ion from 1 makes this species unstable relative to the less compressed bromocarbenium ion. The latter ion is also a far more favorable precursor for the covalent *exo-cis*-dibromides which must otherwise be formed in a front-side displacement reaction.

## Experimental Section

Vapor-phase chromatographic analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph utilizing a Hewlett-Packard peak integrator. Preparative vapor-phase chromatography was conducted on a Varian 920 chromatograph fitted with a 4 ft, 20% Carbowax 20 M on Chrom P column.

$^1H$ NMR spectra were measured on JEOL MH-100 and Varian EM-390 instruments, and $^{13}C$ NMR spectra on a JEOL FX-60; chemical shifts are expressed in parts per million downfield from internal tetramethylsilane.

Mass spectra were obtained on a Finnigan OWA 1020 GC-MS-DS spectrometer using an ionization potential of 70 eV. Melting points are uncorrected.

Reagent grade tetrahydrofuran was dried over Na–benzophenone and distilled prior to use. Acetonitrile and benzene were predried over 3-Å molecular sieves.

Thin-layer chromatography was carried out on precoated plastic plates (silica gel with UV indicator) from Brinkmann Instruments, Inc. Thick-layer chromatography was performed on glass plates coated with silica gel (20 × 20 cm, 1000-$\mu$m thickness) from Analabs, Inc.

The preparative additions of $Br_2$,[19] HBr, HCl, $H_2O$, and $CH_3OH$ to 1 and 2 and the competitive reactions of both olefins using bromine, HBr, and HCl have been reported elsewhere.[1]

**Cycloaddition of ASNB (2) with Phenyl Azide.** A solution of 2 (0.10 g, 0.0006 mol) in anhydrous ethyl ether (20 mL) was treated with phenyl azide (0.135 g, 0.0011 mol, 1.8 equiv) at room temperature. After 3 days of stirring, $^1H$ NMR indicated almost complete conversion of ASNB to the cycloadduct. Solvent evaporation gave a residue which was purified by thick-layer chromatography (3:1, petroleum ether/ether) to yield pure triazoline adduct (0.14 g, 79%): $^1H$ NMR ($CDCl_3$) $\delta$ 0.9–2.2 (12 H, m, $-CH_2-$), 2.5–2.9 (4 H, m, bridgehead H's), 6.8–7.0 (1 H, m, phenyl), and 7.1–7.3 (4 H, d, phenyl); $^{13}C$ NMR ($CDCl_3$) $\delta$ 23.97, 24.68, 25.72, 37.87, 38.39, 39.50, 40.54, 44.57, 45.74, 74.07, 100.18, 113.96, 121.76, 129.29, and 140.21.

**Cycloaddition of SSNB (1) with Phenyl Azide.** The procedure of Paquette and Carr was followed.[2]

**Competitive Kinetics with Phenyl Azide.** A 15-mL round bottom flask was charged with 2 (20.6 mg), 1 (22.5 mg, 0.2689-mmol total olefin), hexadecane (26.9 mg), and methylene chloride (3 mL). After thorough stirring, the mixture was treated with phenyl azide (52.4 mg, 0.4398 mmol), and the flask was immersed in an oil bath which had been preheated to 50 °C. Aliquots were removed at 15, 70, and 125 min for analysis by vpc. As the aliquots were removed from the reaction mixture, they were transferred to small sample vials which contained 15-mg portions of triphenylphosphine dissolved in $CH_2Cl_2$. The phosphine reacted immediately with the phenyl azide, causing the sample to take on a greenish color, which completely disappeared within 15 min.

VPC analysis was performed on a 6 ft, 5% W98 Hiplate column programmed to 100 → 200 °C at 1 min initial time and 39°/min ramp rate.

**Kinetics with a Series of Phenyl Azides.** The series of substituted phenyl azides (R = H, *p*-Me, *p*-MeO, *m*-MeO, *m*-Br, *p*-Br, *m*-$NO_2$, and *p*-$NO_2$) was prepared[7] and made to react with SSNB (1), in order to obtain the corresponding triazoline adducts.

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(19) Paquette, L. A.; Ohkata, K.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 3303.

**Table IV. Concentration Determinations in SSNB–Azide Reactions**

| substituent | wavelength, nm | t, min. | $E_t - E_0$ | $\epsilon_{adduct} - \epsilon_{azide}$ | (adduct) × $10^5$ |
|---|---|---|---|---|---|
| *p*-MeO | 325 | 40 | 0.097 | 6991 | 1.39 |
| *p*-Me | 315 | 30 | 0.150 | 8418 | 1.78 |
| H | 320 | 36 | 0.175 | 6725 | 2.60 |
| *m*-MeO | 320 | 20 | 0.128 | 8261 | 1.55 |
| *p*-Br | 320 | 50 | 0.235 | 10040 | 2.34 |
| *m*-Br | 315 | 30 | 0.340 | 9503 | 3.58 |
| *m*-Br | 315 | 32 | 0.059 | 9503 | 0.621 |
| *m*-$NO_2$ | 390 | 30 | 0.291 | 1058 | 27.50 |
| *m*-$NO_2$ | 390 | 40 | 0.135 | 1058 | 12.76 |
| *p*-$NO_2$ | 390 | 20 | 1.388 | 10207 | 13.60 |

In addition the triazoline adducts with R = H, *m*-$NO_2$, and *p*-$NO_2$ were prepared from both ASNB (**2**) and 10-oxa-2,3-benzo-SSNB (**3**). The triazoline adducts were required since the preferred method of following the kinetics of the addition reactions involved UV spectrometry, for which the molar extinction coefficients of both the phenyl azides and the addition products needed to be determined.

The kinetic studies were done according to the procedure described for the same reaction with norbornene.[7] Equal volumes of ethyl acetate solutions containing the olefin and the substituted phenyl azide were mixed in a cuvette that was kept at 30 °C in the cavity of the UV spectrometer. The temperature in the cavity was constant at ca. 30 °C. The reactions were followed by observing the light absorption at constant wavelength. The wavelengths were chosen at the maximum difference between the absorptivity of phenyl azides and the triazoline adducts, and the conversions were not higher than ca. 3%. Hence the rate constant is expressed as $k = \Delta[\text{triazoline}]/([\text{azide}][\text{olefin}]\Delta t)$. Under the conditions of the experiments, the triazoline adducts were stable. The addition of the azide to the olefin is a clean reaction, as evidenced by the presence of isosbestic points.

**Reaction of *m*-Chloroperbenzoic Acid with 1 and with 2.** The MCPBA epoxidations of **2**[12] and **1**[20] have already been described.

**Competitive Kinetics with MCPBA.** A mixture of **2** (20.6 mg), **1** (20.1 mg, 0.2539-mmol total olefin) and hexadecane (25.1 mg) in methylene chloride (15 mL) was cooled to 0 °C under nitrogen with an ice bath. MCPBA (97% pure, 57.9 mg, 0.335 mmol) was added to the mixture in one portion, and aliquots were removed from the flask every few minutes for vpc analysis. The aliquots were quenched with a mixture of 10% $Na_2SO_3$ and 10% $NaHCO_3$ to convert MCPBA to sodium *m*-chlorobenzoate.

**Competitive Kinetics with Acetone in the Presence of Di-*tert*-butyl Peroxyoxalate.** A mixture of **2** (23.2 mg), **1** (23.3 mg, 0.290-mmol total olefin), ethylbenzene (internal standard, 26.4 mg), acetone (3mL), and di-*tert*-butyl peroxyoxalate (69.6 mg, 0.297 mmol) was stirred at room temperature under nitrogen. Vpc analysis (10 ft, 5%) indicated that the isomeric olefins were converted to a mixture of epoxides and acetonyl adducts.

When the solvent (acetone) was purged with nitrogen for 30 min before the radical initiator was added, the formation of epoxides was completely suppressed.

**Reaction of 1 with Ozone.** This reaction has been carried out as described by Paquette and Carr.[2]

**Reaction of 2 with Ozone.** The olefin (0.40 g, 0.0025 mol) was dissolved in pentane (150 mL), and the mixture was cooled to 0 °C. Ozone was then bubbled through the solution until a blue color persisted in the reaction mixture (approximately 45 min). The ozone purging was then stopped and the mixture warmed to room temperature. After nitrogen was bubbled through the solution to remove excess ozone, the blue color disappeared. The reaction mixture was filtered to give a white solid, **13** (0.47 g, 90%): mp 212–214 °C (sample detonated at 215 °C); $^{13}C$ NMR (20) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 7218.
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**Table V. Melting Points and UV Extinction Coefficients of Triazoline Adducts at Wavelengths Used in Rate Studies**

| R | mp, °C | wavelength used, nm | $\epsilon$ |
|---|---|---|---|
| | from **1** | | |
| H | 127–30 | 320 | 6800 |
| *p*-MeO | 131–134 | 325 | 7120 |
| *p*-$NO_2$ | 165–170 (dec) | 390 | 10587 |
| | | 390 | 10090 |
| *m*-$NO_2$ | 160 (dec) | 390 | 1085 |
| *m*-Br | 170–2 | 315 | 9600 |
| *m*-MeO | 131–4 | 320 | 8350 |
| *p*-Br | 193–5 (dec) | 320 | 10150 |
| *p*-Me | 156–8 | 315 | 8515 |
| | from **2** | | |
| H | 126–8 | 320 | 6890 |
| *p*-$NO_2$ | ~150 (dec) | 390 | 8715 |
| *m*-$NO_2$ | 139–42 | 390 | 1082 |
| | from **3** | | |
| H | 151–4 | 320 | 6250 |
| | | 350 | 490 |
| *m*-$NO_2$ | 214–7 (dec) | 390 | 894 |
| *pNO*$_2$ | 275 (dec) | 390 | 6220 |

($CDCl_3$) $\delta$ 217.8, 112.53, 52.95, 30.53, 28.39. Note: Off-resonance indicates overlapping peaks at 52.95 ppm.

**Generation of Diketone 14.** A heterogeneous mixture of the diperoxide **13** (0.40 g) and $PtO_2$ (50 mg) in 10 mL of 50:50 ethanol/acetone was stirred vigorously under hydrogen atmosphere at room temperature. After 1 h the mixture turned greenish blue, and the solution was let stir for 23 h. After filtration through Celite to remove the catalyst, solvent evaporation in vacuo gave crude diketone **14**. Purification by column chromatography (25 g of neutral silica gel) with methylene chloride as elution solvent gave pure diketone **14**.

**Competitive Experiment with 1 and 2 in the Presence of Ozone (–78 °C) Using Hexadecane as Internal Standard.** A mixture of 33.0 mg of **2**, 34.2 mg of **1**, and 22.0 mg of hexadecane (internal standard) was dissolved in pentane. The solution was cooled to –78 °C in an acetone–dry ice bath. Then a slow stream of ozone was bubbled through the solution for a short period of time, after which the reaction mixture was analyzed by vpc (Conditions: 6 ft 5% SE-30 column; program 100-0-39/min-225-10). Because the products precipitate out of the solution, some acetone was added to ensure a clear solution containing starting material and products. This procedure of bubbling ozone through the solution was repeated a few times until most of the olefin was converted to products. The experiment was carried out in duplicate.

**Kinetic Measurements.** The determination of the rate constant for the addition of phenyl azide to *syn*-sesquinorbornene illustrates the method used for the studies of all the substituted phenyl azides with the cyclic olefins. In each case the molar extinction coefficients $\epsilon$ were determined for the pure phenyl azide ($\epsilon_x$ in the equations) and the triazoline product $\epsilon_z$, at a convenient wavelength chosen to maximize the difference between $\epsilon_x$ and $\epsilon_z$. In all cases the olefin was transparent at this wavelength. Therefore the initial optical density $E_0$ and the optical density $E_t$ at a kinetic point are equal to

$$E_0 = x_0\epsilon_x + z_0\epsilon_z = x_0\epsilon_x$$

since $z_0 = 0$

$$E_t = x_t\epsilon_x + z_t\epsilon_z = x_t\epsilon_x + (x_0 - x_t)\epsilon_z$$

since $z$ is equal to the decline in $x$. When terms are combined it is seen that

$$z_t = \frac{E_t - E_0}{\epsilon_z - \epsilon_x}$$

while $x_t = x_0 - z_t$.

In general, the rate constants were calculated by fitting the usual second-order rate equation to the concentrations as a function of time. In the azide additions, however, the UV method was so sensitive that adequate rate measurements were obtained with 1% or less change in the concentrations of the reactants, and the rate constants could be determined by the zero-order approximation

$$k = \frac{1}{t}\left(\frac{\Delta z}{x(x + c)}\right)$$

where $c = [\text{olefin}]_0 - x_0$.

The rate constants for the substituted phenyl azides are shown in Table III, and some of the data used in determining them are given in Table IV.

**Acknowledgment.** We thank the Robert A. Welch Foundation and the National Science Foundation for support of this work.

**Supplementary Material Available:** Tables of IR and NMR spectral data of the triazoline adducts reported in Table V (3 pages). Ordering information is given on any current masthead page.

# Synthesis and Electrophilic Cleavage of Some Verbenylstannanes

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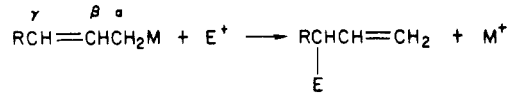
Trifluoroacetolysis of the allylic *cis*- and *trans*-verbenylstannanes yields a mixture of *cis*- and *trans*-δ-pinenes, confirming regiospecific γ-substitution. Analysis of the product distribution confirms the view that any inherent preference for γ-anti substitution (anti-$S_E'$ process) is not so strong that steric effects on both reagent approach and product development cannot influence the balance between syn and anti stereocourses. Sulfur dioxide insertion (chloroform solvent) proceeds readily with the *trans*-stannane to provide the rearranged (tertiary) "δ-pinenylsulfinate" in a stereospecific syn fashion (syn-$S_E'$ process). *cis*-Verbenylstannane is less reactive but is transformed to the same sulfinate. The verbenylstannanes were acquired by trimethyl- and triphenylstannylation (with (trimethyltin)lithium and (triphenyltin)lithium in tetrahydrofuran) of predominantly (~90%) *trans*-verbenyl chloride.

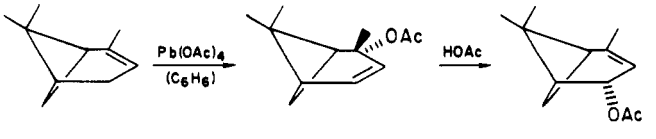
Electrophilic substitution of allyl derivatives of main group metals is a topic of considerable interest and quite attractive because of its γ-regiospecificity as shown below.[1,2] As part of a general program concerned primarily



with the formation and cleavage of allylic derivatives of silicon and tin, we have reported on the stereochemical aspects of these reactions with cyclohex-2-enyl derivatives.[3,4] While this work was progressing, the absence of a stereochemical generality with respect to the $S_E'$ process (electrophilic substitution with allylic rearrangement) became obvious,[1,4] and examination of further structurally diverse allylic systems was required to identify the chief factors regulating stereochemistry. It appeared to us that terpene-based systems, because of their availability and diverse structural features and possiblity of transformation (via allylic metal derivatives) into useful derivatives,[2] warranted examination. In this paper we discuss the characterization of some verbenylstannanes and details of their substitution reactions with acid and sulfur dioxide, while subsequent reports will focus on the carvone- and piperitone-derived allylic stannanes and silanes.[5] While this work was proceeding, we became aware that Russian workers, particularly Kashin and Reutov,[6] had prepared and examined some tin derivatives in this series. Our studies of the verbenylstannanes, while more extensive, agree generally with the Russian findings.

## Results and Discussion

α-Pinene was converted to predominantly *trans*-verbenol according to the procedure described by Whitham.[7] This involves reaction with lead tetraacetate (in benzene) to form *cis*-3-pinen-2-yl acetate which undergoes ready allylic isomerization (with acetic acid) to *trans*-verbenyl acetate, followed by saponification. (eq 1). In our hands,




(1)

α-pinene, $[\alpha]_D$ +51° (c, 5.31, $CH_3OH$), was converted in 38% overall yield to an alcohol mixture ($[\alpha]_D$ +116.6° (c 2.07, $CHCl_3$)) which comprised *trans*-verbenol (87%) and

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