21) should be correctly represented by structure **3**. This has been confirmed by X-ray crystallography.[22] The structure **3** includes all the chiral centers of erythronolide A in the proper absolute configuration. The otherwise irrelevant center at C_9 must be inverted before efficient cyclization of the related hydroxy acid can be achieved (see ref 2). This is being investigated.

Registry No. 3, 79832-53-4; **5**-(β-Ac), 82281-54-7; **5**-(α-Ac), 82294-14-2; **6**, 82294-13-3; **7**, 39947-42-7; **8**, 82335-24-8; **9**, 82294-16-4; **10**, 82281-55-8; **11**, 82281-56-9; **12**-(β-OH), 82281-57-0; **12**-(α-OH), 82335-25-9; **13**-(β-isopropenyl), 82281-58-1; **13**-(α-isopropenyl), 82335-26-0; **14**, 82281-59-2; **15**, 82335-27-1; **16**, 82335-28-2; **17**-(5-α-OH), 82281-60-5; **17**-(5-β-OH), 82335-29-3; **18**-(β-isopropenyl), 82281-61-6; **18**-(α-isopropenyl), 82335-30-6; **19**-(β-isopropenyl), 82281-62-7; **19**-(α-isopropenyl), 82335-31-7; **20**, 82281-63-8; **21**, 82281-64-9; 5-methylcyclopentadiene, 96-38-8; (+)-α-pinene, 7785-70-8; 2-bromopropene, 557-93-7; 2-propenyllithium, 3052-45-7; erythronolide A, 26754-37-0.

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(*E*)-Bicyclo[3.3.1]non-1-ene

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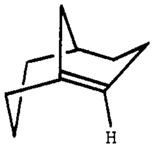
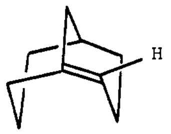
Received March 18, 1982

Cyclic alkenes with trans carbon–carbon double bonds have been characterized as either stable products or short-lived intermediates, depending on the ring size.[1-3] Our group and that of Marshall independently synthesized bicyclo[3.3.1]non-1-ene, **1**, a compound that is stable enough to permit isolation and purification but much more reactive than olefins lacking strain.[4a,b] In its isolable form, **1** has the zusammen configuration, (*Z*)-**1**, as it is related in structure and stability to *trans*-cyclooctene.[4b] The geometrical isomer of **1**, the entgegen form, (*E*)-**1**, must possess appreciable strain energy because the double bond is constrained trans in the six-membered ring. Thus Kim and White failed to obtain the corresponding syn-elimination product (*E*)-**1** upon thermal decomposition of the endo-sulfoximine **2a**. However, pyrolysis of the exo-epimer **2b** gave a good yield of alkene (*Z*)-**1**.[4c]

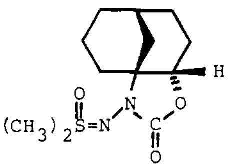


(*Z*)-1

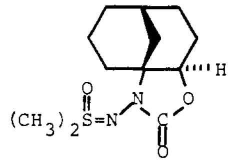
1



(*E*)-1

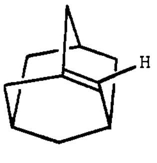


2a

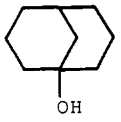


2b

On the basis of empirical force-field calculations, Schleyer et al. noted a relationship of alkene–parent alkane strain-energy differences (olefinic strain, OS) and the chemical stability of several bridgehead alkenes.[5] They classified the bridgehead alkenes according to their calculated olefinic strains (kcal/mol) as isolable ($OS < 17$), observable ($17 < OS < 21$), or unstable ($OS > 21$). Adamantene, **3** (calculated OS = 39.5 kcal/mol), which resembles (*E*)-**1** (calculated OS = 44.2 kcal/mol) in having an additional methylene bridge, has been detected chemically as a transient intermediate and has been observed spectrophotometrically in a cryogenic matrix.[6] The existence of *trans*-cycloalkenes with six or seven ring carbons has been demonstrated in the photochemical addition of alcohols to cyclic olefins.[7] Marshall and Kropp have attributed the stereochemical outcome of some of these reactions to an ionic addition proceeding by protonation of the highly strained photoisomer by the alcohol. Marshall and Faubl irradiated alkene **1** in water–dimethoxyethane with *p*-xylene as a triplet photosensitizer and found 30% production of the bridgehead alcohol, **4**.[4a] By analogy to earlier results, they proposed that the photohydrolysis occurred through (*E*)-**1**. In this report we present definitive evidence for the intermediacy of (*E*)-**1** in both direct and sensitized photomethanolysis of alkene (*Z*)-**1**.



3



4

Alkene (*Z*)-**1** has an ultraviolet absorption at longer wavelengths than ordinary olefins (λ_{max} (pentane) 206 nm, ϵ 7500), with a tail extending above 230 nm. This permits direct irradiation of **1** through a Vycor filter (50% transmittance at 235 nm). In a typical experiment, 192 mg of alkene (*Z*)-**1** was added to a quartz tube[8] containing 2.0 mL of dry methanol in which 3 mg of sodium had been dissolved. Making the solution basic in this manner avoided acid-catalyzed methanol addition. In a control experiment in which no radiation reached the sample, no reaction was observed. The solution was degassed by several freeze–thaw cycles and irradiated with a 450-W Hanovia lamp for 10 h at 25 °C. Gas-phase chromatography (15% OV-101) revealed 32%[9] production of 1-methoxybicyclo[3.3.1]nonane, **5**. The remainder consisted largely of unreacted olefin (65%), some dimers (*m/e* 244), and small amounts of polymer. Ether **5** was identified by comparing its 360-MHz proton NMR, IR, and mass spectra[10]

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[8] Prior to each irradiation, the quartz tube was soaked in 20% methanolic NaOH, washed with concentrated ammonia, and dried.

[9] All product yields were determined by gas chromatography relative to tetradecane as an internal standard.

[10] All NMR spectra were obtained on a Bruker WM-360 spectrometer (360 MHz). Mass spectra were run on a Finnigan 4023 GC/MS incorporating a Finnigan/INCOS 2300 data system.

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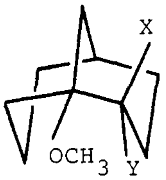
to those of a sample prepared from **1** by hydrogen chloride catalyzed methanolysis.

A similar photochemical experiment using methanol-*O-d* (99% min) as the solvent provided 25% of methyl ether **5nd** after 11 h.



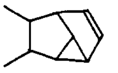
5, X = H; Y = H
5nd, X = H; Y = D
5xd, X = D; Y = H

The mass spectrum of **5nd** had a molecular ion peak at *m/e* 155 (91% d_1 incorporation) and gave a proton NMR closely similar to that of **5**. Reaction of alkene (*Z*)-**1** with methanol-*O-d* catalyzed by deuterium chloride gave **5xd** quantitatively. Both **5nd** and **5xd** gave identical mass spectra with molecular ions of *m/e* 155 and peaks of nearly equal intensity at *m/e* 111 and 112 (M − 44, 43), consistent with the loss of either one of the three-carbon bridges. The 360-MHz ^1H NMR spectra were also quite similar. However, the ^2H NMR[11] spectra of the two products were distinctly different. Ether **5nd** produced a single resonance peak at δ 1.78[12] (half-width of 5.01 Hz), whereas **5xd** displayed a single resonance at δ 1.48 (half-width of 5.06 Hz). The spectra showed no cross contamination of epimers.

The difference in deuterium chemical shifts of **5nd** and **5xd** arises from incorporation at different loci on C-2. Deuteration on the less hindered (external) face of the double bond of (*Z*)-**1** must give rise to the 2-exo-deuterium ether, **5xd**. The deuterium should be axial in the chair–chair conformer of **5xd**, which is in accord with it having the higher field chemical shift (δ 1.48). It follows that the deuterium in the photochemical product, **5nd**, is endo and equatorial. This marked stereochemical contrast is explained as resulting from deuteration by methanol-*O-d* on the external face of alkene (*E*)-**1**.

Direct photomethanolysis of (*Z*)-**1** in mixtures of CH_3OD and CH_3OH permitted determination of the kinetic isotope effect for protonation of (*E*)-**1** by methanol ($k_H/k_D = 8.0$). This result indicates that proton transfer is about half completed in the transition state.

Photosensitized methanolysis of alkene (*Z*)-**1** was also accomplished by using molar excesses of benzene and *p*-xylene as photosensitizers, but the yields of ether **5** were lowered due to the formation of alkene–arene adducts. The ^2H NMR spectra again showed stereospecific formation of **5nd** when methanol-*O-d* was the solvent. One of the four benzene–alkene adducts (*m/e* 200) was purified by gas chromatography and showed a proton NMR spectrum similar to that of **6**, isolated by Wilzbach and Kaplan in the photoaddition of *cis*-2-butene to benzene. The cycloadducts with benzene are tentatively assigned structures **7** and/or **8**, stereochemistry unknown. Further study of the photochemistry of bridgehead alkenes is in progress.



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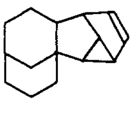

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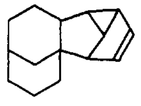

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Registry No. 1Z, 54674-58-7; **1E**, 82509-63-5; **5**, 63160-90-7; deuterium, 7782-39-0.

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(11) Deuterium spectra were obtained at an irradation frequency of 55 MHz. A 1% solution of $CDCl_3$ in carbon tetrachloride served as the solvent.

(12) Measured in reference to δ 7.24 for $CDCl_3$.

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A Simple Relationship between Carbocation Lifetime and Reactivity–Selectivity Relationships for the Solvolysis of Ring-Substituted 1-Phenylethyl Derivatives[1]

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We describe here the experimental demonstration of a predicted[2] V-shaped reactivity–selectivity curve for reactions of 1-phenylethyl derivatives, I (Chart I). The azide–solvent selectivity, k_{az}/k_s, M^{-1} (Figure 1) decreases sharply, crosses a narrow "borderline" region, and increases with increasing σ^+ as the reaction mechanism changes. These changes exhibit a simple correlation with the lifetime of the 1-phenylethyl carbocation.

Values of k_{az}/k_s (Figure 1, 50:50 trifluoroethanol/water, v/v, $\mu = 0.5$, $NaClO_4$) were determined by product analysis with HPLC.[3] The value of $k_{MeOCOCH_2S^-}/k_s$ instead of k_{az}/k_s was used for ia because the azide adduct is unstable; k_{az}/k_{RS^-} was found to be 1.8 for iic, and ratios of $k_{az}/k_{RS^-} = 0.2$–0.03 have been reported for triarylmethyl carbocations.[4,5]

The dependence of k_{obsd} on azide concentration for the reactions of substituted 1-phenylethyl chlorides in acetonitrile/water (Figure 2) undergoes a change from zero order for compounds to the left of the selectivity break ($\sigma^+ \le -0.32$) to first order for compounds to the right of the break ($\sigma^+ \ge -0.08$). The plots are linear for azide concentrations up to 0.6 M. The fraction of azide adduct product was found to agree within experimental error with the fractional rate increase in the presence of azide for all reactions that are first order in azide; i.e., >80% of the azide adduct is formed by the pathway that is first order in azide.

A change in the dependence of selectivity on the leaving group is also observed at the selectivity break. Substrates to the left of the break show constant selectivities for large changes in leaving group (open circles and squares, Figure 1), while substrates to the right of the break exhibit selectivities which are dependent on the leaving group (closed symbols, Figure 1). The right-hand limb in Figure 1 is drawn through points for substituted 1-phenylethyl chlorides.

We account for the decreasing and increasing limbs in Figure 1 as follows. The zero-order dependence of k_{obsd} on azide concentration, through azide concentrations that give at least 40% yield of azide adduct, demonstrates a stepwise mechanism and a carbocation intermediate for substrates to the left of the selectivity break. The decreasing selectivity with increasing carbocation reactivity contrasts with the constant azide selectivity (k_{az}/k_s) of 10^6 M^{-1} observed for the more stable triarylmethyl carbocations.[6,7] The different reactivity–selectivity behavior can be rationalized if the rate constant k_{az} is activation limited for triarylmethyl carbocations and diffusion limited for 1-phenylethyl carbocations.[8-11] A downward selectivity break is expected when

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[1] Supported by grants from the National Science Foundation (PCM-7708369) and the National Institutes of Health (GM20888). Dr. Richard was supported by a grant from the National Institute of Health (AM 07251).

(2) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161–169.

(3) Products were separated over a reverse-phase octadecylsilane chromatography column (10 μm, Waters Associates) with MeOH/HOH.

(4) A value of k_{az} of 5×10^6 M^{-1} s^{-1} for the reaction of the trianisylmethyl carbocation was reported: Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536–3544. A value of k_{RS^-} of 7×10^7 for the reaction of $HOCH_2CH_2S^-$ with the same carbocation was reported: Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318–7323.

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