Photochemical generation and ¹H NMR detection of alkyl allene oxides in solution¹

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Abstract: Irradiation of substituted 5-alkyl-4,5-epoxyvalerophenones leads to the formation of alkyl allene oxides that, in some cases, are sufficiently long-lived to be detected at room temperature by ¹H NMR spectroscopy. Absolute life-time measurements show that the size of the alkyl group has a significant influence on the reactivity of the allene oxide, with *tert*-butyl allene oxide having a lifetime of 24 h in CD₃CN at room temperature that is considerably longer than the 1.5 h lifetime of the ethyl allene oxide. The allene oxides react rapidly with water to give α -hydroxyketones. The mechanism involves nucleophilic attack to the epoxide carbon to give an enol, which can also be detected as an intermediate by ¹H NMR spectroscopy.

Key words: allene oxides, mechanisms, absolute reactivity, kinetics, photochemistry.

Résumé : L'irradiation de 5-alkyl-4,5-époxyvalérophénones substituées conduit à la formation d'oxydes d'alkyle et d'allène qui, dans certains cas, ont des temps de vie suffisamment longs pour qu'on puisse les détecter, à la température ambiante, par spectroscopie RMN du ¹H. Des mesures de temps de vie absolus montrent que la taille du groupe alkyle joue un rôle important sur la réactivité de l'oxyde d'allène; le temps de vie de l'oxyde de *tert*-butyle et d'allène, dans le CD₃CN et à la température ambiante, est de 24 h ce qui est beaucoup plus long que celui de l'oxyde d'éthyle et d'allène qui n'est que d'une heure et demie. Les oxydes d'allène réagissent rapidement avec l'eau pour conduire à la formation d' α -hydroxycétones. Le mécanisme implique une attaque nucléophile du carbone de d'époxyde pour conduire à un énol qu'on peut aussi détecter comme intermédiaire par spectroscopie RMN du ¹H.

Mots clés : oxydes d'allène, mécanismes, réactivité absolue, cinétique, photochimie.

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Introduction

Allene oxides (1-3) have been studied by theoretical and experimental chemists for several decades. Much of the original interest in these compounds came from their close relationship with cyclopropanones, which are structural isomers of allene oxides (4-9). More recently, they have been implicated as intermediates in the conversion of fatty acids to cyclopentenones and α -ketols in some plants and marine organisms (10, 11), and have also been used as intermediates in synthetic organic chemistry (11–20).

While allene oxides are generally considered to be reactive species, some are sufficiently stable to be isolated (21-24). This has allowed for the spectroscopic analysis of some allene oxides, and has also led to qualitative conclusions concerning the effect of structure on allene oxide stability (1). The chemistry of allene oxides that are too unstable to be isolated has also been examined through the analysis of products from reactions in which the allene oxides are present as undetected, transient intermediates (1, 2). These stud-

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ies have shown that the reactions of allene oxides are dominated by rearrangement to cyclopropanones and addition of nucleophiles to give α substituted ketones.

Some absolute rate constants for the reactions of allene oxides in solution have been measured (25–27), but this remains one area of allene oxide chemistry that has not yet been extensively examined. Quantitative data concerning the effect of structure, solvent, and other parameters on the reactivity of allene oxides can be readily obtained from absolute reactivity measurements, and this information can lead to mechanistic details that are often difficult to determine from product-based studies. In the present work, we describe results concerning the absolute reactivity of some monoalkyl substituted allene oxides. A key feature of this work is the use of a photochemical method to rapidly generate these allene oxides. As a result, more reactive and previously undetected allene oxides could be examined directly by ¹H NMR spectroscopy.

Results and discussion

The photochemical method used to generate the allene oxides in this work is based on the Norrish type II reaction of substituted 4,5-epoxyvalerophenones 1 (eq. [1]). With these substrates, excitation was expected to lead to efficient triplet formation followed by rapid intramolecular hydrogen transfer to generate a 1,4-biradical that fragments to give the desired allene oxide 2, together with acetophenone.



Initial experiments were carried out using the precursor 1a $(R = (CH_3)_3C)$, which would give the *tert*-butyl allene oxide 2a that has been isolated by other methods and fully characterized by NMR spectroscopy (23, 28). ¹H NMR analysis showed that irradiation of 1a (ca. 20% depletion) in CD₃CN at room temperature led to the formation of prominent new signals³ including doublets at 4.34 ppm (J = 3.2 Hz) and 4.28 ppm (J = 3.2 Hz) and a singlet at 3.53 ppm (Fig. 1A), as well as a singlet at 2.60 ppm. The signals at 4.34, 4.28, and 3.53 ppm are the same as those previously assigned to the tert-butyl allene oxide (23, 28), with the doublets being assigned to the vinyl protons, and the singlet at 3.50 ppm to the epoxide proton; the signal at 2.60 ppm corresponds to the methyl protons of acetophenone. Thus, the NMR spectra obtained after irradiation clearly showed that fragmentation leading to allene oxide formation as shown in eq. [1] is occurring.

The same method was applied to the generation of other allene oxides with less bulky groups at the epoxide carbon that have until now eluded direct detection. For precursor 1b $(R = (CH_3)_2CH)$, the NMR spectrum after irradiation in CD₃CN showed the formation of overlapping doublets at 4.30 ppm and a doublet at 3.57 ppm (Fig. 1B). The signals at 4.30 and 3.57 ppm are similar to those observed for the tert-butyl allene oxide, which is consistent with the assignment of these signals to the isopropyl allene oxide 2b. Furthermore, the signal at 3.57 ppm is now a doublet, rather then the singlet that appears for the *tert*-butyl allene oxide, as expected for the isopropyl 2b allene oxide in which the epoxide proton is located adjacent to the CH of the isopropyl moiety. For precursor 1c (R = CH₃CH₂), irradiation led to the formation of new peaks at 4.29 and 3.71 ppm (Fig. 1C). Again, these chemical shifts and the nature of the splitting are consistent with the assignment of these new peaks to the ethyl allene oxide 2c.

Irradiation of precursor 1d in CD₃CN led to no detectable amounts of the parent allene oxide 2d. A signal at 2.60 ppm owing to the formation of acetophenone was observed, which suggests that allene oxide formation as outlined in eq. [1] had occurred. Thus, our inability to detect allene oxide 2d is likely due to its high reactivity. To further establish that 2d was indeed generated, irradiation of 1d was carried out with 5% D₂O in acetonitrile. Under these conditions, a prominent singlet at 4.01 ppm and triplet at 2.09 ppm were observed. These signals correspond to 1-*d*-3-deuteroxy-2propanone (29), which is the expected product upon addition of D₂O to allene oxide 2d. Thus, the parent allene oxide is generated upon irradiation of 1d, but even in dry acetonitrile it is too short-lived to be detected under our reaction conditions. Since our experimental conditions involved 5 min of Fig. 1. ¹H NMR spectra obtained 4 min after irradiation of precursors (A) 1a, (B) 1b, and (C) 1c in CD_3CN at room temperature.



Fig. 2. Integrated area of the vinyl protons of the *tert*-butyl (\bigcirc), isopropyl (\blacksquare), and ethyl (\bigcirc) allene oxides in CD₃CN at 25 °C measured as a function of time after irradiation of the corresponding precursors. The solid lines represent the line-of-best-fit calculated using a first-order rate expression.



irradiation followed by ca. 3 min to acquire the initial 1 H NMR spectrum, the lifetime of the parent allene oxide must be less 8 min in neat CD₃CN at room temperature.

Not surprisingly, the allene oxides 2a-2c in neat CD₃CN at room temperature also were not stable, as illustrated by the decrease in the integrated areas of the ¹H NMR signals of the vinyl protons as a function of time in Fig. 2. These data can in principle be used to determine the absolute reactivity of the allene oxides; however, given the difficulties in measuring accurate values for the integrated areas, the data were not sufficiently good to distinguish between a first-order decay or a second-order decay of the allene oxides. Nonetheless, the data clearly show a substantial difference in the reactivity of the allene oxides as a function of the size of

³Other weak resonances owing to unidentified by-products were also evident in the ¹H NMR spectrum.

Table 1. First-order rate constants for the decay of allene oxides 2a-2d in CD₃CN (25 °C).

| R | k_{decay} (s ⁻¹) |
|-----------------|---------------------------------------|
| tert-Butyl (2a) | $(1.2\pm0.2) \times 10^{-5}$ |
| Isopropyl (2b) | $(2.4\pm0.4) \times 10^{-5}$ |
| Ethyl (2c) | $(1.9\pm0.2) \times 10^{-4}$ |
| H (2d) | >10 ⁻³ |

the alkyl group, with the isopropyl allene oxide 2b being considerably more reactive than the *tert*-butyl allene oxide 2a, and the ethyl allene oxide 2c showing even greater reactivity. This order of reactivity as a function of the size of the alkyl group is nicely consistent with conclusions made previously (2, 24) that bulky groups directly attached to the epoxide ring serve to enhance the kinetic stability of allene oxides.

While the decay traces in Fig. 2 fit equally well to firstand second-order rate expressions, a measure of the differences in reactivity can be estimated by comparing rate constants obtained using a first-order fit (Table 1). These results show that the *tert*-butyl allene oxide **2a** and the isopropyl allene oxide decay slowly with rate constants of 1.2×10^{-5} and 2.4×10^{-5} s⁻¹, respectively, which differ only by a factor of two. On the other hand, the ethyl allene oxide **2c** decays about an order of magnitude more quickly with a rate constant of 1.9×10^{-4} s⁻¹. In addition, based on our inability to detect the parent allene oxide, we can estimate that it decays with a rate constant $>10^{-3}$ s⁻¹. The parent allene oxide therefore decays at least 10 times more rapidly than the ethyl derivative, and at least 100 times more rapidly than the bulky *tert*-butyl and isopropyl allene oxides.

The actual reaction of the allene oxides in neat CD_3CN remains unclear. One possibility is that the allene oxides rearrange to the substituted cyclopropanones. However, no ¹H NMR signals corresponding to cyclopropanones could be observed after complete decay of the allene oxides, nor could signals owing to the alkene that would be generated by rapid loss of CO from the cyclopropanone. In fact, no distinct signals were observed to grow as the allene oxides decayed, suggesting that the allene oxides may polymerize or react with solvent to give material difficult to characterize.

Allene oxides are well-known to react with nucleophiles to give α substituted ketones (2), but little is known about the absolute rate constants associated with this nucleophilic addition process. In the present work, the effect of adding D₂O was examined by monitoring the decay of the allene oxides signals in various D₂O–CD₃CN mixtures. Since D₂O was expected to add rapidly to the allene oxides, irradiation of the precursors was carried out in neat CD₃CN, and an ¹H NMR spectrum obtained to ensure that allene oxide formation had occurred. An appropriate amount of D₂O was then added, followed rapidly by the acquisition of a series of spectra. In this way, allene oxide decaying with rate constants less than 0.01 s⁻¹ could readily be monitored.

In these experiments, the reduction in the intensity of the vinyl protons of the allene oxides as a function of time fit well to a first-order rate expression giving the pseudo-first-

Fig. 3. Rate constants for the decay of the *tert*-butyl (\bigcirc), isopropyl (\bigcirc), and ethyl (\blacksquare) allene oxides in CD₃CN as a function of D₂O content (25 °C).



order rate constants that are plotted as a function of D₂O content in Fig. 3. These data clearly show that all three allene oxides decayed considerably more quickly upon the addition of water; however, the reactivity of the allene oxides toward D₂O was strongly dependent on the nature of the alkyl substituent. Thus, in the presence of the *tert*-butyl group, the rate constants for allene oxide decay hardly changed at low D₂O contents, and the *tert*-butyl allene oxide could still be easily observed in 40% D₂O where it decayed with a rate constant of 6.7×10^{-4} s⁻¹. This is in contrast to the results obtained with the isopropyl allene oxide whose decay increased dramatically even in the presence of small amounts of D₂O, and could no longer be observed at D₂O contents >10%. The ethyl allene oxide was even more reactive, with the rate constant for decay increasing 10-fold upon going from neat CD₃CN to 3% D₂O in CD₃CN. At higher D₂O contents, the ethyl allene oxide could no longer be observed.

Nucleophilic addition of D₂O to the allene oxides was expected to lead to the formation of the corresponding α hydroxyketone, and this material was indeed observed by ¹H NMR as the final stable product in the reaction of the allene oxides with D₂O. Two mechanisms for this nucleophilic addition can be envisioned: addition can occur via an S_N1-like mechanism characterized by initial breaking of the epoxide C-O bond followed by addition of the nucleophile, or via an S_N2-like mechanism where the nucleophile directly adds to the intact epoxide ring (eq. [2]). In both cases, the initial product is an enol that then tautomerizes to the more stable ketone form. The formation of the enol intermediate is supported by the sequence of ¹H NMR spectra in Fig. 4. Figure 4A shows the isopropyl allene oxide after irradiation in CD₃CN, but before the addition of D₂O. Five minutes after the addition of 10% D₂O, the allene oxide signals were reduced (Figs. 4B and 4C) and eventually replaced by resonances at 3.9 and 4.1 ppm that correspond to the expected (30) chemical shifts of the vinyl protons of the enol intermediate. A doublet at 3.65 ppm was also observed that can be assigned to the proton on the carbon bearing the hydroxy group of the enol. The enol signals were then replaced by a





doublet at 3.9 ppm (Fig. 4D), attributed to the proton at the α position of the expected α -hydroxyketone product⁴ (29).

While formation of the enol intermediate is consistent with the mechanism shown in eq. [2], its observation was surprising given the high reactivity of most simple enols (31). Two factors may contribute to the unusually long lifetime. First, most absolute rate constant measures for the ketonization of enols have been measured in wholly aqueous solutions; in the 10% aqueous conditions used to observe the enol in Fig. 2B, the enol ketonization process may be somewhat slowed. In fact, in experiments carried out at higher water contents of 30%, the enol could no longer be observed, despite the more rapid disappearance of the allene oxide. Second, the α -hydroxy group may play a role in reducing the reactivity of the enol form by hydrogen bonding. Such hydrogen bonding may reduce the electron density at the enolic OH, thus reducing the overall electrophilicity and the rate constant for addition of a proton to the enolic carbon-carbon double bond.

The effect of structure on the absolute reactivity of the allene oxides with water can also provide some insight into the mechanism of the nucleophilic addition reaction. In particular, rate constants for addition of the nucleophile in the $S_N 2$ mechanism should show a dependence on structure, while in the $S_N 1$ -like mechanism, little difference in reactiv-

ity upon going from *tert*-butyl to ethyl should be observed. As shown in Fig. 3, a fairly dramatic structural effect is observed, which leads to the conclusion that nucleophilic addition occurs via the $S_N 2$ mechanism.

Conclusions

Our results clearly show that photogeneration of allene oxides by the Norrish type II fragmentation of 4-alkyl-4,5epoxyvalerophenones leads to formation of simple alkyl substituted allene oxides. Since the allene oxides are generated rapidly, this method allows for the detection of allene oxides that had not previously been observed, and for absolute rate constants to be measured. The use of this photoreaction should be compatible with the generation of broader series of simple alkyl allene oxides, and also with the use of a fast reaction technique like flash photolysis to examine the reactivity of very short-lived allene oxides. Experiments to address those issues are currently under way.

Experimental

Preparation of precursors

Precursors **1a–1d** were prepared by addition of the enolate of acetophenone to the appropriate 1-bromo-2-alkene derivative to give the corresponding 1-phenyl-pent-4-en-1-one, followed by epoxidation using m-chloroperbenzoic acid. In general, the procedure involved the addition of 1 equiv. of lithium diisopropylamine to acetophenone (1.5 g) in dry THF (15 mL) under an argon atmosphere at -78 °C and stirring for 20 min. One equivalent of 1-bromo-4,4-dimethyl-2pentene (32) (for 1a), 1-bromo-4-methyl-2-pentene (33) (for 1b), 1-bromo-2-pentene (33) (for 1c), or 1-bromo-2-propene (Aldrich) (for 1d) was then added, and the mixture allowed to warm up to room temperature over a period of 20 h. The solution was diluted with ether and washed with saturated aqueous ammonium chloride and sodium chloride. The organic layer was dried and the solvent removed under reduced pressure. The crude enone was purified by silica gel column chromatography using 50% dichloromethane in hexanes as the eluant.

Epoxidation was carried out by adding 1.5 equiv. of purified *m*-chloroperbenzoic acid to the enone in CH_2Cl_2 . The mixture was stirred for 1.5 h at room temperature. After washing with 5% sodium hydroxide and evaporation of the solvent, the crude product was purified by silica gel column chromatography (20% ethyl acetate in hexanes).

1-Phenyl-6,6-dimethyl-4,5-epoxyheptan-1-one (1a)

¹H NMR (ppm) δ: 7.45–8.05 (multiplet, 5H), 3.14 (t, 2H), 2.92–2.97 (m, 1H), 2.56 (d, 1H), 2.08–2.22 (m, 1H), 1.77–1.91 (m, 1H), 0.92 (s, 9H). ¹³C NMR (ppm) δ: 25.7, 26.5, 30.6, 54.5, 67.1, 127.9, 128.5, 133.0, 136.6, 199.0. HR-MS calcd.: 232.1463; found: 232.1459.

1-Phenyl-6-methyl-4,5-epoxyheptan-1-one (1b)

¹H NMR (ppm) δ: 7.45–8.05 (multiplet, 5H), 3.15 (t, 2H), 2.85–2.91 (m, 1H), 2.53–2.57 (d of d, 1H), 2.10–2.23 (m, 1H), 1.78–1.92 (m, 1H), 1.45–1.62 (m, 1H), 1.01 (d, 3H),

⁴The final product also shows the CH₂D protons as a triplet at 2.1 ppm and the methyl groups as doublets at 1.0 and 0.7 ppm.

0.96 (d, 3H). ¹³C NMR (ppm) δ: 18.3, 18.9, 26.4, 30.3, 34.5, 56.8, 64.5, 127.9, 128.5, 133.0, 136.6, 199.0. HR-MS calcd.: 218.1307; found: 218.1299.

1-Phenyl-4,5-epoxyheptan-1-one (1c)

¹H NMR (ppm) δ: 7.45–8.05 (multiplet, 5H), 3.15 (t, 2H), 2.82–2.87 (m, 1H), 2.71–2.77 (m, 1H), 2.12–2.25 (m, 1H), 1.78–1.91 (m, 1H), 1.53–1.64 (m, 2H), 1.00 (t, 3H). ¹³C NMR (ppm) δ: 9.7, 24.9, 26.3, 34.5, 57.5, 60.2, 127.9, 128.5, 133.0, 136.6, 199.1. HR-MS calcd.: 204.1150; found: 204.1146.

1-Phenyl-4,5-epoxypentan-1-one (1d) (34)

¹H NMR (ppm) δ : 7.45–8.05 (multiplet, 5H), 3.20 (t, 2H), 3.10–3.17 (m, 1H), 2.81 (t, 1H), 2.55–2.58 (m, 1H), 2.16–2.24 (m, 1H), 1.80–1.89 (m, 1H). ¹³C NMR (ppm) δ : 26.8, 34.4, 47.3, 51.5, 127.9, 128.5, 133.1, 136.6.

Irradiation of precursors and determination of rate constants

About 10 mg of **1a-1d** were dissolved in 0.750 mL of CD_3CN (Aldrich) in a quartz cuvette (3 mm × 1 cm × 3 cm). The solution was bubbled with nitrogen for 10 min and then irradiated with 308 nm light (60 mJ/pulse, 8 ns pulse) from a Lambda-Physik excimer laser operating at 5 Hz for 5-10 min or with a high-pressure mercury lamp for 15–30 min. Immediately after irradiation, the solution was transferred to an NMR tube and the spectrum obtained using a Bruker AC-250 MHz spectrometer (probe temperature 25 °C). To obtain kinetic data, NMR spectra were obtained at specific time intervals after irradiation. The time intervals varied depending on the lifetime of the allene oxides, but generally six to ten spectra were obtained. The peak area or intensity corresponding to the vinyl protons of the allene oxides was measured in each spectrum (relative to a small amount of CH₂Cl₂ added as an internal standard). These areas or intensities were plotted as a function of time, and rate constants extracted by nonlinear least-squares fitting of the data to a first-order exponential equation.

For studies involving the addition of water, irradiation of the precursor was carried out in the same way in neat CD_3CN . The ¹H NMR spectrum was then obtained to ensure allene oxide formation had taken place. A desired amount of D_2O was then added, followed by the acquisition of further NMR spectra at appropriate time intervals. Rate constants were determined in the same way as described in the previous section for reaction in neat CD_3CN . In all cases, the ¹H NMR spectra of the final stable product matched closely the published spectra of the corresponding α -hydroxy ketones (29).

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