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SINGLET OXYGEN AND TRIAZOLINEDIONE ADDITIONS TO α,β-UNSATURATED SULFOXIDES

Takeshi AKASAKA, Yoshihisa MISAWA, Midori GOTO,# AND Wataru ANDO*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

and

#National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

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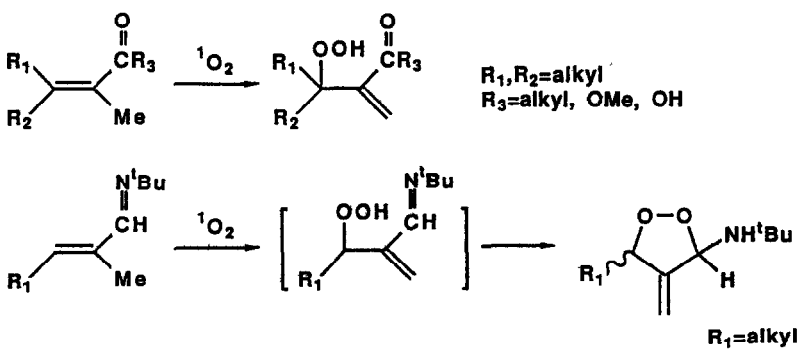
Abstract: The reaction of singlet oxygen with 2-methyl-3-phenylsulfinyl-2-butene (**1a**) and *E*-2-phenylsulfinyl-2-butene (**1b**) gives the corresponding allyl alcohols (**2a** and **2b**) after reduction with dimethyl sulfide. α,β-Unsaturated sulfoxides with s-*trans* conformation failed to proceed the ene-type oxidation but afforded S-oxidation products. On the other hand, 4-methyl-1,2,4-triazoline-3,5-dione (MeTAD) reacted with α,β-unsaturated sulfoxides (**1a** and **1b**) and *E*-2-ethylidenethiolan-1-oxide (**1g**) to give the corresponding allyl triazolidines as ene-type products.

Introduction

The "ene" reaction of singlet oxygen ($^1O_2$) with olefins has been extensively studied because of its synthetic utility[1] and the mechanistic interest[2] associated with this reaction. Despite these intensive investigations, there are only a few examples of the oxidation of olefins which are substituted with electron-withdrawing groups.[3] Since $^1O_2$ is shown to be weakly electrophilic,[4] the fact that electron-deficient olefins are unreactive toward $^1O_2$ is not surprising. Recently, the photooxygenation of α,β-unsaturated ketones,[3a-c,3h] esters,[3d] carboxylic acids,[3e] and aldimines[3f,3g] has been reported to afford the corresponding allylic hydroperoxides by preferential abstraction of allylic hydrogens geminal to the carbonyl and imino groups (Scheme I). As a part of our continuing synthetic and mechanistic interest in $^1O_2$ reaction of olefins,[3f,3g,5] we have investigated the $^1O_2$ oxygenation of α,β-unsaturated sulfoxides. On the other hand, 4-substituted-1,2,4-triazoline-3,5-dione (TAD) exhibits a wide range of reactivity

Scheme I



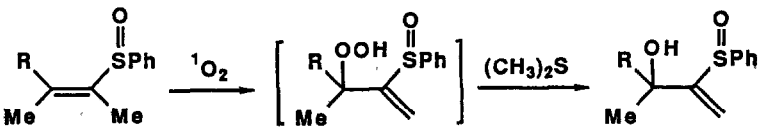
and reaction types analogous to some of $^1O_2$ reactions.[6] An attempted addition to s-*cis*-α,β-unsaturated sulfoxides proceeded via preferential abstraction of hydrogen geminal to the sulfinyl group. We provide new insight on singlet oxygenation for unsaturated compounds.

Results and Discussion

Singlet Oxygen Addition to α,β-Unsaturated Sulfoxides

In a typical experiment, photooxygenation of 2-methyl-3-phenylsulfinyl-2-butene (**1a**, 0.5M) was carried out at 15°C for 7 hr in benzene with tetraphenylporphine (TPP, $5x10^{-3}$M) as a sensitizer by use of two 500-W tungsten-halogen lamps. After reduction with dimethyl sulfide, the reaction mixture was separated by preparative HPLC. The corresponding allyl alcohol **2a** was obtained regiospecifically in 80% yield. Very similar results were obtained with E-2-phenylsulfinyl-2-butene (**1b**) under the same conditions. The photooxygenation followed by preparative HPLC led to the isolation of the corresponding allyl alcohol **2b**. Compound **2** might be formed by reduction of hydroperoxy sulfoxide **3** (Scheme II). No reaction takes place in the absence of light or a sensitizer. Moreover, the photooxygenation was inhibited by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.3 eq), a $^1O_2$ quencher.[7] These results clearly demonstrate that $^1O_2$ is the active oxygen species responsible for the photooxygenation.

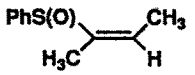
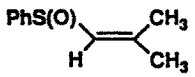
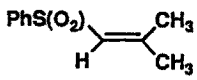
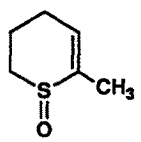
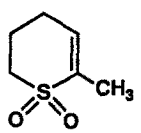
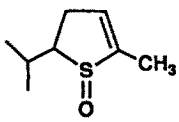
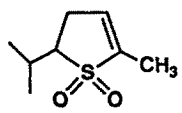
Scheme II



1a ; R=Me **1b ; R=H** **3a** **3b** **2a** **2b**

To elucidate the scope and limitation of the photooxygenation, a series of sulfoxides, *Z*-2-phenyl-sulfinyl-2-butene (**1c**), 1-phenylsulfinyl-2-methylpropene (**1d**), 2-methylthiacyclohex-2-ene-1-oxide (**1e**), and 2-methyl-5-isopropylthiacyclopent-2-ene-1-oxide (**1f**), were also submitted to the reaction with $^1O_2$ (Table 1). As shown in Table 1, the electronic and/or conformational effects may be important in accounting for the differences in reactivities of α,β-unsaturated sulfoxides. The β-values[1] as a measure of reactivity of the sulfoxides toward $^1O_2$ are shown in Table 2. In the oxidation of α,β-unsaturated ketones, [3c,3d] it has been reported that there is no correlation between ionization potentials of the ketones and reactivities toward $^1O_2$, and that electronic effects are not important.[3c] The similar results were also obtained in the photooxidation of α,β-unsaturated aldimines.[3f,3g] The one-electron oxidation potentials (E_{ox} vs SCE) of the sulfoxides (**1a-f**) are ranged from +1.9 to +2.3V in 0.1M n-Bu_4NClO_4/CH_3CN solution. Since a good linear relationship is well known between ionization potentials of electron donors and frequencies of charge-transfer absorption bands in complexes of tetracyanoethylene (TCNE) with electron-donors,[8] the charge-transfer frequencies in complexes of TCNE with the α,β-unsaturated sulfoxides (Table 2) were measured. It was found that there is no correlation between oxidation potentials and reactivities toward $^1O_2$, which means that electronic effects do not influence the overall reactivity. The large difference in the

Table 1. Reaction of $^1O_2$ with α,β-Unsaturated Sulfoxides

substrate	products and yields(%)[a]
1a	2a (80)
1b	2b[b] (46)
 1c	recovered 1c (quant.)
 1d	 4d (58)
 1e	 4e (64)
 1f	 4f (90)

a) conversion yields.
b) the ratio of isomers is 2:3.

Table 2. Comparison of Reactivities of α,β-Unsaturated Sulfoxides

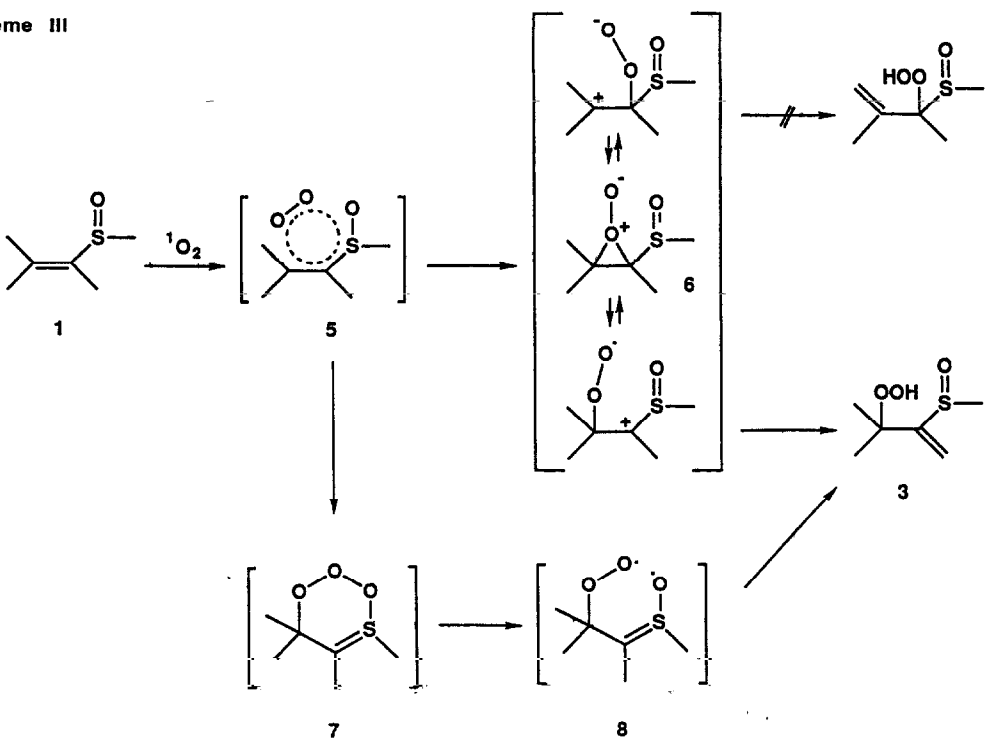
substrate	β-value[a]	E_{ox}(V) vs SCE	$\nu_{max}(cm^{-1})$[b]
1a	11	+1.90	23,500
1b	26	+2.28	23,900
1c	100<	+2.23	23,900
1d	100<	+2.26	24,100
1e	100<	+1.93	23,900
1f	100<	+1.87	23,700

a) β-values were determined using linalool (β = 0.18) as the standard; $\beta = k_d/k_r$.
b) frequencies for CT absorptions in complexes of TCNE with 1.

β-values for s-*cis*- and s-*trans*-α,β-unsaturated sulfoxides may account for the preferential formation of the oxidation products. The conformational difference in reactivity toward $^1O_2$ between *E*- and *Z*-α,β-unsaturated sulfoxides, **1b** and **1c**, is presumably due to the cis-effect well known in $^1O_2$ ene reaction of alkyl-substituted olefins.[2b] α,β-Unsaturated sulfoxides, **1e** and **1f**, which are structurally confined to be the s-*trans* conformation react with $^1O_2$ to afford the corresponding sulfones,[9] but not allylic hydroperoxides as the ene-products. Formation of allylic hydroperoxide arises from the s-*cis* conformation. The reaction of $^1O_2$ with α,β-unsaturated sulfoxides shows preferential abstraction of allylic hydrogen geminal to the sulfoxide functionality. The reaction of $^1O_2$ with **1d** which does not bear methyl group on the carbon atom bonded to the sulfoxide functionality did, however, not give an ene product, but S-oxidation product **4d** on prolonged oxidation.

Based on these observations, the following mechanism is proposed in which $^1O_2$ might form an exciplex intermediate **5** with α,β-unsaturated sulfoxides, similar to the case of phenyl-substituted alkenes[10] and α,β-unsaturated aldimines,[3f,3g] followed by formation of a zwitterionic intermediate **6** forcing geminal hydrogen abstraction (Scheme III). In the intermediates such as **6**, the β-hydrogen atom next to the sulfinyl group is more acidic and should thus be preferentially removed, similar to the case of α,β-unsaturated aldimines.[3f,g] An alternative intermediate such as a trioxene intermediate **7**[3c] may be conceivable.[11] Formation of trioxene **7**, followed by rupture of the O-O bond, may lead intermediate **8**, forcing geminal hydrogen abstraction. This reaction path is similar to that proposed in the oxidation of α,β-unsaturated ketones.[3c]

Scheme III



Triazolinedione Addition to α,β-Unsaturated Sulfoxides

To a stirred solution of α.β-unsaturated sulfoxides **1** in methylene chloride (0.1M) was added 1.0 equiv of a solution of MeTAD in methylene chloride (0.1M) at room temperature under argon atmosphere and then the reaction mixture was refluxed. When the red color of MeTAD had disappeared, the resulting products were separated by preparative HPLC. The corresponding ene product was isolated in high yields. In Table 3 are listed the α,β-unsaturated sulfoxide **1a**, **1b**, **1d-f**, and *E*-2-ethylidenethiolan-1-oxide (**1g**), which were allowed to react with MeTAD (1.0 equiv) at reflux temperature in methylene chloride. The substrates **1a**, **1b**, and **1g** were regiospecifically converted to the ene adducts **9** in good yields. α,β-Unsaturated sulfoxides **1d-f** did not react with MeTAD even after several daysat the reflux temperature in methylene chloride. The reaction of MeTAD with sulfoxides **1** shows a strong preference for sulfoxides capable of adopting an s-*cis* conformation. This is true for every entry in Table 3, whereas substrates **1e** and **1f**, which are confined to be s-*trans* conformation, are unreactive. The similar requirement of s-*cis* structure in the MeTAD addition to enones was noted earlier by Hunter and Sciloff,[12] and Hoye et al.[6j] The same is true for successful ene reactions of $^1O_2$ with α,β-unsaturated ketones, esters, carboxylic acids, aldimines, and sulfoxides. Addition of MeTAD to sulfoxide **1b** proceeded regiospecifically to give two diastereomers **9b** and **9b'**. The stereochemistry of **9b'** was assigned by means of X-ray crystal analyses (Fig). Although $^1O_2$ oxygenation of **1g** gave only a complex mixture of products, MeTAD addition to **1g** afforded **9g** regio- and stereospecifically. The reaction of MeTAD with the substrate **1d** did not give an ene product. Based on these observations, it is conceivable that the reaction mechanism in MTAD addition to α,β-unsaturated sulfoxides involves the same type of reaction sequence in the case of singlet oxygenation as shown in Scheme III.

The present study shows the first ene-type reaction of α,β-unsaturated sulfoxides with $^1O_2$ and MeTAD to afford 2-sulfinyl allyl alcohol derivatives and their aza anlogues. It is clear that s-*cis* compounds react with $^1O_2$ and MeTAD, but s-*trans* conformers do not.

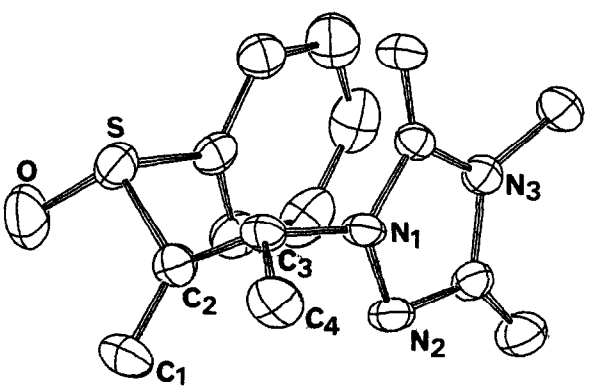
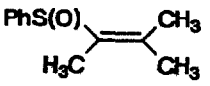
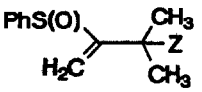
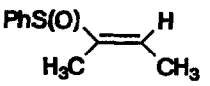
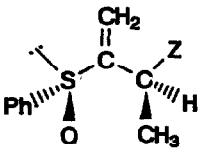
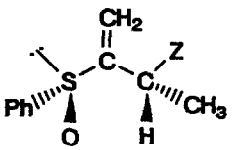
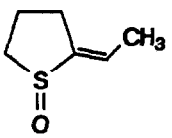
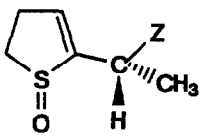
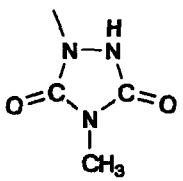


Fig. ORTEP drawing of **9b'**

Table 3. Reaction of MeTAD with α,β-Unsaturated Sulfoxides.

substrate		products and yields(%)	
	1a		9a (75)
	1b		
		9b (64)	9b' (26)
	1g		9g (73)

Z = 

Experimental

All melting points are uncorrected. IR spectra were recorded with a Hitachi 260-50 infrared spectrometer, ^{1}H-NMR spectra recorded with a JEOL JNM-PMX60SI spectrometer, ^{13}C-NMR spectra recorded with a JEOL JNM-FX100 spectrometer (solvent, deuteriochloroform and carbon tetrachloride; tetramethylsilane as an internal standard), and UV spectra with a Shimadzu UV365 spectrophotometer. Mass spectral data were obtained on a Hitachi RMU-6M mass spectrometer and exact mass data on a JEOL LMS-D300 mass spectrometer. Gas chromatography was done on an Hitachi 163 gas chromatograph equipped with a FID detector, 4 mm x 2 m glass column, and 3% OV-1 on Uniport HP. Gel permeation chromatography (preparative HPLC) was performed on a

series of JAIGEL 1H and 2H columns with a flow of chloroform on a LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd. The light source was two 500-W tungsten-halogen lamps. Irradiations were carried out in Pyrex tubes at 15°C while oxygen was passed through. Benzene was distilled in the presence of lithium aluminum hydride before use. Dichloromethane was washed with water, dried over calcium chloride and then distilled in the presence of calcium hydride. TPP (STREM CHEMICALS) and dimethyl sulfide (TOKYO KASEI) were used as received. DABCO was used after purification by sublimation. TCNE was recrystallized from chlorobenzene and sublimed at 125°C/4mmHg. MTAD[6j] and sulfoxides, **1a-c**[13,14] and **1g**[15] were prepared according to the literature procedure. **1b** and **1c** were separated and purified by preparative HPLC. Sulfoxides, **1d**,[13] **1e**,[16] and **1f**[17] were prepared by oxidation of the corresponding sulfide with *m*-chloroperbenzoic acid. **1d**: oil; IR(NaCl) ν 1030 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.19-7.74(m,5H), 5.88-6.09(m,1H), 2.14(brs,3H), 1.84 (brs,3H) ppm; ^{13}C-NMR($CDCl_3$) δ 149.2(s), 145.0(s), 132.1(d), 130.4(d), 129.2(d), 124.0(d), 25.2(q), 20.2(q) ppm; m/e 180(M^+). Exact Mass Calcd for $C_{10}H_{12}OS$: 180.0608. Found: 180.0613. **1e**: oil; IR(NaCl) ν 1010 cm-1; ^{1}H-NMR($CDCl_3$) δ 5.93-6.13(m,1H), 2.81-3.08(m,2H), 1.70-2.52(m,4H), 2.13(brs,3H) ppm; ^{13}C-NMR ($CDCl_3$) δ 136.7(s), 130.3(d), 46.2(t), 25.5(t), 19.7(q), 13.6(t) ppm; m/e 130(M^+). Exact Mass Calcd for $C_6H_{10}OS$: 130.0467. Found: 130.0460. **1f**: oil; IR(NaCl) ν 1020 cm-1; ^{1}H-NMR($CDCl_3$) δ 6.03-6.30(m,1H), 3.15-3.23(m,3H), 2.08-2.21(m,3H), 1.05-1.30(m,7H) ppm; ^{13}C-NMR($CDCl_3$) δ 145.1(s), 144.0(s), 137.1(d), 132.0(d), 77.9(d), 68.4(d), 37.0(t), 34.2(t), 29.8(d), 26.4(d), 22.5(q), 20.8(q), 14.0(q), 12.9(q) ppm; m/e 158 (M^+). Exact Mass Calcd for $C_8H_{14}OS$: 158.0764. Found: 158.0756. The isomeric mixture was not separated but showed a 1:1 ratio.

Physical Properties of Sulfoxides

Cyclic voltammograms of substrate **1** were obtained on 0.1 M n-Bu_4NClO_4/CH_3CN solution (vs SCE; scan rate, 200 mV/s; Hokuto Denko Ltd., Potentiostat/Galvanostat Model HZ-301). Oxidation potentials (E_{ox})are shown in Table 2.

β-Values[1] (k_d/k_r; k_d=rate constant for solvent deactivation of $^1O_2$; k_r=rate constant for chemical reaction of the substrate) were determined using linalool (β=0.18) as the standard by means of GC analysis and are listed in Table 2.

UV measurements of formation of complexes between TCNE and sulfoxide were carried out as follows. To a methylene chloride solution of the sulfoxide (0.1 M) was added an equimolar amount of TCNE in methylene chloride under argon at room temperature. The resulting complexes were immediately analyzed by UV spectroscopy. Frequencies of charge-transfer complexes obtained are shown in Table 2.

Photooxygenation of Sulfoxides

In a typical experiment, **1a** (0.5 M) was dissolved in benzene with TPP ($5x10^{-3}$ M) as sensitizer. After addition of dimethyl sulfide to the reaction mixture, the oxygenated products were separated by preparative HPLC. **2a** was obtained in 60% yield (conversion yield 80%), accompanied with recovered **1a** (25%). **2a**: oil; IR($CDCl_3$) ν 3300, 1030 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.41-7.80(m,5H), 6.02(d,1H,J=1.4Hz), 5.76(d,1H,J=1.4Hz), 3.34 (brs,1H), 1.39(s,3H), 1.21(s,3H) ppm; ^{13}C-NMR($CDCl_3$) δ 161.5(s), 144.2(s), 131.0(d), 129.0(d), 126.0(d), 115.0(t), 73.3(s), 31.6(q), 30.9(q) ppm; m/e 210(M^+). Exact Mass Calcd for $C_{11}H_{14}O_2S$: 210.0715. Found:210.0715. **2b**: oil; IR($CDCl_3$) ν 3300, 1035 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.41-7.87(m,5H), 6.02(brs,1H), 5.85-5.91(m,1H), 4.21-4.67(m,1H), 2.54-3.20(m,1H), 1.34 and 1.21(d,3H,J=7.1Hz) ppm; ^{13}C-NMR($CDCl_3$) δ

156.7(s), 142.0(s), 131.3(d), 129.4(d), 124.9(d), 118.2(t), 116.5(t), 65.4(d), 64.5(d), 23.0(q), 21.6(q) ppm; m/e 196(M^+). Exact Mass Calcd for $C_{10}H_{12}O_2S$: 196.0598. Found: 196.0578. The isomeric mixture was not separated but showed a 2:3 ratio. **4d**: oil; IR($CDCl_3$) ν 1305, 1140 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.43-8.04(m,5H), 6.0-6.20(m,1H), 2.16(d,3H,J=1.5Hz), 1.89(d,3H,J=1.5Hz) ppm; ^{13}C-NMR($CDCl_3$) δ 154.2(s), 142.4(s), 132.9(d), 129.1(d), 127.1(d), 126.3(d), 27.1(q), 19.2(q) ppm; m/e 196(M^+). Exact Mass Calcd for $C_{10}H_{12}O_2S$: 196.0557. Found: 196.0535. **4e**: IR(NaCl) ν 1300, 1110 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 5.97-6.13(m,1H), 3.07-3.28(m,2H), 2.22-2.45(m,4H), 2.05(brs,3H) ppm; ^{13}C-NMR($CDCl_3$) δ 137.1(s), 132.8(d), 50.8(t), 25.1(t), 20.9(t), 13.5(q) ppm; m/e 146(M^+). **4f**: IR(CCl_4) ν 1305, 1140 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 6.19-6.27(m,1H), 2.38-3.03(m,3H), 2.05-2.22(m,3H), 1.25-1.40(m,1H), 1.25(d,3H,J=7.0Hz), 1.04(d,3H,J=7.0Hz) ppm; ^{13}C-NMR($CDCl_3$) δ 140.9(s), 130.8(d), 64.9(d), 29.7(t), 28.2(d), 20.9(q), 20.1(q), 9.1(q) ppm; m/e 174(M^+).

Reaction of Sulfoxides with MTAD

Into a 50 ml round-bottomed flask was placed 1 mmol of **1a** in 10 ml of methylene chloride. While stirring at room temperature, 1 mmol of MTAD in 10 ml of methylene chloride was added dropwise under argon. The resulting solution was refluxed until the red color of MTAD had disappeared. The products were separated by preparative HPLC. **9a** was obtained in 75% yield. **9a**: mp 130-132°C; IR($CDCl_3$) ν 3350, 1750, 1720, 1680, 1030 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.50-7.70(m,5H), 6.06(d,1H,J=2.0Hz), 5.94(d,1H,J=2.0Hz), 2.89(s,3H), 1.68 (s,3H), 1.60(s,3H) ppm; ^{13}C-NMR($CDCl_3$) δ 158.1(s), 155.1(s), 153.6(s), 141.8(s), 131.7(d), 129.9(d), 125.9 (d), 119.5(t), 63.1(s), 26.3(q), 25.9(q), 25.0(q) ppm; m/e 307(M^+). Anal Calcd for $C_{14}H_{17}N_3O_3S$: C, 54.70; H, 5.57; N, 13.67. Found: C, 54.44; H, 5.56; N, 13.65. **9b**: mp 147-149°C; IR($CDCl_3$) ν 3400, 1750, 1690, 1030 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.41-7.82(m,5H), 6.34(brs,1H), 5.99(brs,1H), 4.62(q,1H,J=7.0Hz), 3.03 (s,3H), 1.33(d,3H,J=7.0Hz) ppm; ^{13}C-NMR(CDCl3) δ 155.2(s), 154.2(s), 152.6(s), 141.4(s), 131.9(d), 129.5 (d), 125.6(d), 118.8(t), 50.1(d), 25.3(q), 15.2(q) ppm; m/e 293(M^+). Exact Mass Calcd for $C_{13}H_{15}N_3O_3S$: 293.0834. Found: 293.0835. **9b'**: mp 167-169°C; IR($CDCl_3$) ν 3400, 1750, 1690, 1025 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.32-7.67(m,5H), 6,32(brs,1H), 6.07(brs,1H), 4.78(q,1H,J=7.0Hz), 2.90(s,3H), 1.42 (d,3H,J=7.0Hz) ppm; ^{13}C-NMR($CDCl_3$) δ 155.1(s), 153.0(s), 152.9(s), 140.5(s), 131.5(d), 129.4(d), 124.9 (d), 124.3(t), 50.6(d), 25.0(q), 17.1(q) ppm; m/e 293(M^+). Exact Mass Calcd for $C_{13}H_{15}N_3O_3S$: 293.0834. Found: 293.0812. **9g**: mp 179-181°C; IR($CDCl_3$) ν 3350, 1750, 1720, 1025 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 6.52-6.70(m,1H), 5.17-5.37(m,1H), 3.06(s,3H), 2.81-3.69(m,4H), 1.55(d,3H,J=7.0Hz) ppm; ^{13}C-NMR ($CDCl_3$) δ 154.56(s), 153.98(s), 148.48(3), 139.64(d), 51.30(t), 50.49(d), 32.47(t), 25.21(q), 16.21(q) ppm; m/e 243(M+). Exact Mass Calcd for $C_9H_{13}N_3O_3S$: 243.0678. Found: 243.0640.

X-ray Crystal Analysis of 9b'

Intensity data were collected on a Rigaku AFC four-circle diffractometer with graphite monochromated Mo-Kα radiation. 1943 reflections obtained within 2θ<55° had intensities greater than 3σ|Fo| and were used for structure analysis. The structure was refined to a value of R=0.055. The molecular structure is shown in Figure. Crystal data of **9b'**: $C_{13}H_{15}N_3O_3S$, monoclinic space group $P2_1/C$, a=6.062(1)A, b=21.132(2)A, c=11.207(2)A, β=109.97(3)°, Z=4.

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Supplementary Material Available: Lists of coordinates and bond distances for **9b'** (14 pages). Ordering information is given on any current masthead pages.

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11. Recently, Foote et al.[3h] reported that in the regioselective singlet oxygenation of 2-cyclopenten-1-one derivatives reactivity toward $^1O_2$ is not solely determined by the conformation of the carbonyl group relative to the olefinic double bond, since even some s-*trans* derivatives are reasonably reactive. This means that the formation of a trioxene intermediate which is geometrically forbidden in the s-*trans* conformers is not responsible for oxidation.

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