Diels-Alder Reactivity of Vinylsulfoxyallenes

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Vinylsulfoxyallenes **3a-c** are prepared from propargylic alcohols in 47-65% yield. Vinylsulfoxyallenes undergo facile [4+2] cycloadditions with methyl triazolidenedione (MTAD) and singlet oxygen to afford phenylsulfinylpyridazines and spirocyclic phenylsulfinyl-2*H*-pyran-3(6*H*)-ones in excellent yields (60-90%). Spirocyclic phenylsulfinyl-2*H*-pyran-3(6*H*)-ones are oxidized to the corresponding phenylsulfones with peracid or can be epoxidized with basic hydrogen peroxide. Spirocyclic pyranone formation is thought to proceed *via* the rearrangement of a labile cyclic peroxide intermediate **14**.

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Introduction.

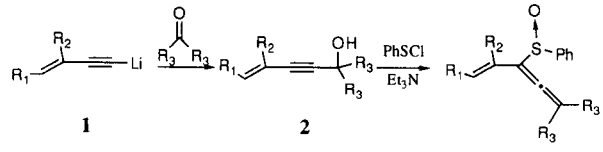
Vinylallenes are important intermediates in organic synthesis [1]. They have been shown to participate in electrocyclic [2], sigmatropic [3], and Diels-Alder reactions [4] for the preparation of several biologically important target molecules. Vinylallenes are receiving increased attention as substrates for transition metal catalyzed carbonylation reactions [5] and as precursors to potent DNA cleaving agents [6].

The use of vinylallenes as the diene component in [4+2] cycloaddition reactions has been shown to provide an excellent entry towards methylene cyclohexenes [7]. The limited studies in this regard have shown that the cycloadditions of vinylallenes proceed with endo selectivity and produce products that are a result of the least sterically hindered approach of the dienophile. Intramolecular cycloaddition reactions of vinylallenes have received the most attention to date. In these reactions, the rigidity of the allene restricts the number of possible conformations in the transition state thereby leading to greater stereoselectivity [8].

The synthetic potential of heteroatom substituted vinylallenes has not been fully explored. As part of our interest in allenic sulfoxides [9], we initiated studies on the [4+2] cycloadditions of vinylsulfoxyallenes with two potent dienophiles, methyl triazolidinedione (MTAD) and singlet oxygen. One of the attractive features of employing vinylsulfoxyallenes in cycloaddition processes is that the sulfoxy group accelerates the cycloaddition, adds control, provides activation of adjacent protons for further manipulation and can be easily removed *via* reductive protocols to provide sulfur free compounds [10]. At the time of this study, only one intramolecular Diels-Alder cycloaddition of a vinylsulfoxyallene had been reported [11].

Results.

Vinylsulfoxyallenes **3a-c** were easily prepared *via* sigmatropic rearrangement of propargylic sulfinates [12]. The required propargylic alcohols **2a-c** in turn were obtained by the addition of the lithio anion **1** to symmetrical ketones [13]. Allenes **3a-c** were purified *via* flash column chromatography, and immediately used in subsequent cycloaddition reactions.



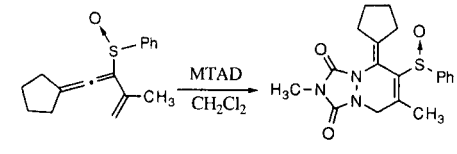
1 **2**

3a: R_1=H; R_2= Me; R_3= $(CH_2)_4$

3b: R_1=R_2=$(CH_2)_4$; R_3= $(CH_2)_5$

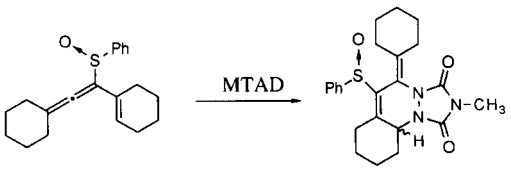
3c: R_1=H; R_2= Me; R_3= CF_3

In order to probe the cycloaddition reactivity of these new dienes, we examined the Diels-Alder reaction with MTAD. The cycloadditions with MTAD occurred at subambient temperatures and were complete within minutes rendering vinylsulfoxypyridazine cycloadducts. A representative example is shown in the conversion of **3a** to vinylsulfoxypyridazine **4** in 90% yield.



3a **4**

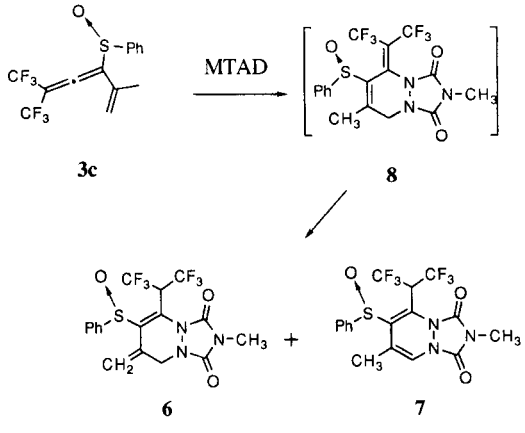
Similarly, **3b** was converted to cycloadduct **5** in 87% yield. The latter was obtained as a 70:30 mixture of diastereomers.



3b **5**

However, the reaction of allene **3c** with MTAD took a different course. The reaction occurred smoothly within minutes at room temperature to give after chromatographic separation a 2:1 ratio of pyridazine **6** and **7** in 57% yield.

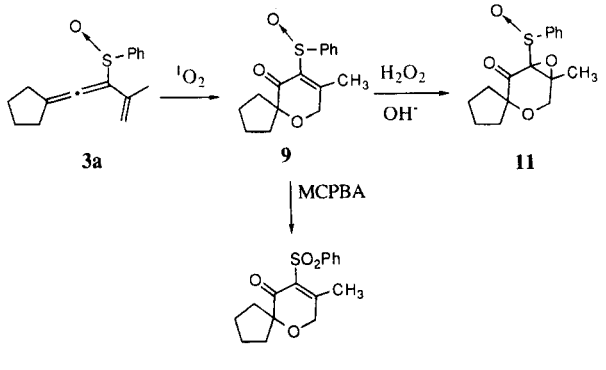
Having successfully conducted cycloadditions with MTAD, the [4+2] cycloaddition reaction with singlet oxygen was next attempted. Photooxygenation at −10° of a methylene chloride solution of **3a** gave pyranone **9** in 95% yield.



3c **8**

6 **7**

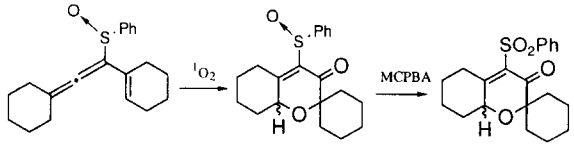
Pyranone **9** proved too unstable for purification *via* silica gel chromatography. Pyranone **9** was converted to sulfone **10** *via* oxidation with *m*-chloroperoxybenzoic acid (MCPBA). Alternatively, **9** could be transformed to epoxypyranone **11** by treatment with basic hydrogen peroxide. Both of these routes provided stable compounds that were fully characterized.



3a **9** **11**

10

In a similar fashion, vinylsulfoxyallene **3b** gave pyranone **12** (isolated as a 1:1 mixture of isomers) when reacted with singlet oxygen. Oxidation of **12** to sulfone **13** was accomplished with one equivalent of MCPBA. Allene **3c** failed to react with singlet oxygen.



3b **12** **13**

Discussion.

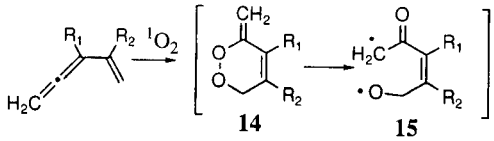
A simple synthesis of vinylsulfoxyallenes was developed using conjugated enynes as initial substrates. The condensation of the lithio anion of enyne **1** with cyclopentanone, cyclohexanone or hexafluoroacetone gave the corresponding propargylic alcohols **2a-c** in high yields (70-85%). These alcohols were converted to the corresponding sulfinates upon reaction with phenylsulfenyl chloride. The sulfinates were generated at −78° and readily underwent a [2,3]-sigmatropic rearrangement to afford allenes **3a-c**. With these vinylallenes in hand, we proceeded to investigate the cycloaddition reactions with triazolinediones and with singlet oxygen.

The initial selection of MTAD as a dienophile was based on its excellent reactivity in [4+2] cycloadditions, and similarity in reactivity to singlet oxygen [14]. The two most important applications of triazolidinediones in organic chemistry are in the characterization of labile dienes and as precursors for azo alkanes [15]. The ease in which cycloadditions occur with these substrates is ascribed to low lying LUMOs [16]. Triazolidinediones have also been used to trap reactive divinyl allenes [17].

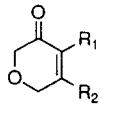
The cycloadditions of **3a-b** occurred as expected producing functionalized pyridazines in high yield. It is noteworthy that no competitive ene reaction products were observed even though allenes **3a-b** contained allylic hydrogens [18]. The cycloaddition of **3b** with MTAD gave **5** as a 70:30 mixture of diastereomers. This ratio was determined *via* nmr by integration of the equatorial and axial hydrogens at C-6. These protons were observed as multiplets centered at δ 4.27 ppm and δ 3.97 ppm respectively. The reaction of **3c** with MTAD, however, provided two unexpected products. The formation of pyridazine **6** and **7** can be rationalized as arising from a isomerization of cycloadduct **8** (what formally corresponds to a 1,5-H-shift). A somewhat related isomerization has been observed in the cycloaddition of phosphine oxide allenes with alkynes [19]. The structure of pyridazine **6** was confirmed *via* proton nmr which showed the gem vinyl protons at δ 5.36 ppm and δ 5.63 ppm.

The singlet oxygenation of vinylallenes is a process that has received limited attention. The first example of this reaction was reported by Gore and Malacria [20]. The reaction is known to yield 2*H*-pyran-3(6*H*)-ones. The mechanism postulated for this transformation involves the homolytic decomposition of vinyl peroxide **14** to generate resonance stabilized diradical **15** which undergoes recombination to pyranone **16**.

Vinyl peroxides similar to **14** are rare but have been postulated as intermediates in the singlet oxygenation of alkenylidenecyclopropanes [21] and in the singlet oxygenation of divinyl allenes [22].



14 **15**



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The unusual rearrangement reaction, **14** to **16**, has not been exploited in synthesis and is worthy of further study. Therefore, we set out to establish the utility of this reaction for the preparation of spirocyclic 2*H*-pyran-3(6*H*)-ones. New approaches for 2*H*-pyran-3(6*H*)-ones are of interest since these substrates have applications as antimicrobial and anticoccidial agents, agrochemical fungicides and serve as precursors to a host of sugars, pheromones and anticancer compounds [23].

The synthesis of spirocyclic pyranone **9** was selected as the initial target. The singlet oxygenation of **3a** proceeded smoothly at $-10°$ to afford **9** as the only product in 90% yield. The structure of **9** was established on the basis of the ^{13}C nmr. The spectrum shows the characteristic resonance for an α,β-unsaturated ketone at δ 193 ppm and two resonances at δ 88.9 ppm and δ 66.5 ppm, corresponding to the spirocyclic carbon and to the methylene carbon adjacent to oxygen. All attempts to purify **9** *via* chromatography led to a complex mixture of decomposition products. This is not surprising since **9** contains two electron withdrawing groups flanking the unsaturated carbons thus making it prone to decomposition *via* conjugate addition reactions. This observation suggested that pyran **9** would readily add hydroperoxide anion and be converted to epoxypyran **11**. Indeed, this conversion was easily accomplished in 65% yield with excess hydrogen peroxide and sodium hydroxide. The ^{13}C nmr of pyran **11** shows two new aliphatic resonances at δ 76.2 ppm and δ 70.4 ppm corresponding to the epoxide ring carbons. In addition, a carbonyl resonance at δ 206 ppm indicates the presence of a nonconjugated ketone. Under the epoxidation conditions, we did not observe oxidation of the sulfoxide moiety. Oxidation to sulfone **10** could be accomplished if MCPBA is used. In this fashion pyran **9** is oxidized to **10** in good yield. Unlike pyran **9**, sulfone **10** was stable towards silica gel chromatography and was purified in this fashion.

The singlet oxygenation reaction of allene **3b** was carried out to establish the utility of the method for the construction of fused and spirocyclic pyrans. The singlet oxygenation of allene **3b** gave a 1:1 mixture of diastereomeric **12** in 88% yield. These diastereomeric products are a result of a non facial selective approach of singlet oxygen to the vinyl allene. Once again, **12** proved unstable for isolation but peracid oxidation to sulfone **13** gave a stable crystalline compound.

All attempts to identify vinyl peroxide intermediates in the singlet oxygenation of allene **3a** *via* low temperature nmr failed [21]. Presumably, the O-O bond homolysis of **14** is too rapid to be detected on the nmr time scale. In an effort to retard the O-O bond homolysis, the singlet oxygenation of allene **3c** was attempted. The rationale being that vinyl peroxide intermediate generated from **3c** would be reluctant to undergo O-O homolysis since this would produce a highly destabilized diradical intermediate. Unfortunately, allene **3c** failed to react with singlet oxygen even after prolonged exposure (48 hours). This observation is in marked contrast with the reactivity of **3c** with MTAD which occurred within minutes. Singlet oxygenation of sulfur containing alkenes have been reported to be sluggish and to require long reaction times [24]. In the case of allene **3c**, the presence of both the phenylsulfinyl and trifluoromethyl groups on the allenic moiety is sufficient to retard the addition of singlet oxygen.

In conclusion vinylsulfoxyallenes undergo facile Diels-Alder cycloadditions with MTAD and singlet oxygen to afford pyridazine and pyran cycloadducts in good yields. We have outlined a simple method that permits the construction of spirocyclic pyran rings and the method should find wide applicability in the synthesis of biologically important pyranone substrates. The utility of these allenes in other cycloaddition processes is the subject of ongoing investigations.

EXPERIMENTAL

Melting points are uncorrected. All reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Flash silica gel chromatography was used to separate and purify the crude reaction mixtures. Infrared (ir) spectra were measured on a Bomen MB 120 spectrometer. Proton nmr spectra were obtained on a GE (300 MHz) and a Bruker (250 MHz). Carbon nmr spectra were obtained on a Bruker (63 MHz). Elemental analyses were carried out by Atlantic Microlab, Atlanta, GA.

1,1,1-Trifluoro-5-methyl-2-trifluoromethyl-5-hexen-3-yn-2-ol (**2c**).

A 250 ml, three necked, round bottomed flask, equipped with a magnetic stirring bar, a gas inlet and a pressure-equalizing dropping funnel, was flushed with dry nitrogen gas. Under a nitrogen gas atmosphere, a solution of 2-methyl-1-buten-3-yne (1.72 g, 26 mmoles) in 20 ml of dry tetrahydrofuran (THF) was introduced. The flask was then cooled with Dry Ice/acetone bath to −77°. A solution of *n*-butyllithium (20 ml, 1.3 *M* in cyclohexane, 26 mmoles) was added dropwise *via* syringe, and the reaction mixture was stirred for 30 minutes. Hexafluoroacetone (*ca.* 6 g, 36 mmoles) was bubbled through the reaction mixture for one hour. The reaction mixture was allowed to stir at room temperature for 16 hours (overnight). The solvent was carefully removed *via* rotary evaporation until most of the THF was removed (the product has a low boiling point and co-distills with THF, therefore, if the solvent is removed completely, the yield is significantly lower). The residue was diluted with ethyl ether and washed with 3 x 25 ml of water. The organic layers were combined and dried with magnesium sulfate, filtered and the solvent evaporated. The volatile residue was distilled *via* Kugel-Rohr distillation (*ca.* bp 50°, 5 mm Hg) to give 2.22 g of 1,1,1-trifluoro-5-methyl-2-trifluoromethyl-5-hexen-3-yn-2-ol (**2c**) in 32% yield, (obtained as a 87:13 mixture with THF); ir (neat): 3410, 3172, 2982, 2884, 2240, 1455, 1274, 1224, 1162, 1075, 957 and 721 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.92 (s, 3H), 5.46 (s, 1H), 5.50 (s, 1H), 5.7 (s, 1H, OH) ppm.

General Procedure for Allene Preparations.

An oven-dried, three-necked, round-bottomed flask equipped with a pressure-equalizing dropping funnel (a syringe can also be used), was charged with a solution of the appropriate propargylic alcohol in methylene chloride. This solution was cooled to −77° and then 1 equivalent of triethylamine was added dropwise. The mixture was stirred for 10 minutes and then, a solution of benzenesulfenyl chloride (1 equivalent) in methylene chloride was added dropwise. Stirring was continued at −77° for 10 minutes and the cooling bath removed to allow the temperature of the reaction to slowly reach room temperature (in some examples the reaction was allowed to proceed overnight). The reaction mixture was quenched with a 1% aqueous hydrochloric acid solution. The organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with water, brine and then dried over anhydrous sodium sulfate. Concentration of the solution under reduced pressure afforded the crude product, which was chromatographed on a silica gel column to give the appropriate allene.

(2-Phenylsulfinyl-3-methyl-1,3-butadienylidene)cyclopentane (**3a**).

Using the general allene procedure, 2 g (1.3 mmoles) of 1-(4-methyl-4-penten-1-ynyl)cyclopentanol, 1.87 g (1.3 mmoles) of benzenesulfenyl chloride and 1.32 g (1.3 mmoles) of triethylamine gave (2-phenylsulfinyl-3-methyl-1,3-butadienylidene)cyclopentane in 47% yield (obtained as a pale yellow oil); ir (neat): 2956, 1935, 1617, 1443, 1047, 748 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.45-2.39 (m, 8H), 1.62 (s, 3H), 5.01 (s, 1H), 5.46 (s, 1H), 7.21-7.56 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 22.1, 26.2, 26.2, 31.0, 31.2, 114.0, 115.1, 118.6, 124.1, 128.2, 130.6, 136.0, 144.3 and 196.1.

Anal. Calcd. for $C_{16}H_{18}OS$: C, 74.37; H, 7.02; S, 12.41. Found: C, 74.37; H, 7.05; S, 12.32.

1-(1-Phenylsulfinyl-2-cyclohexylideneethyl)cyclohexene (**3b**).

Using the general vinylallene procedure, 1 g (0.5 mmole) of 1-[2-(1-cyclohexenyl)ethenyl]cyclohexanol, 720 mg (0.5 mmole) of benzenesulfenyl chloride and 510 mg (0.5 mmole) of triethylamine afforded 1-(1-phenylsulfinyl-2-cyclohexylideethyl)cyclohexane (**3b**) in 55% yield (a pale yellow oil); ir (neat): 2932, 1935, 1581, 1444, 1047, 746 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.23-2.13 (m, 18H), 6.34 (t, 1H), 7.39-7.60 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 21.0, 21.6, 24.3, 24.7, 26.3, 27.2, 28.0, 29.7, 30.1, 112.6, 116.0, 123.8, 125.1, 127.6, 128.4, 129.34, 143.7 and 194.9.

Anal. Calcd. for $C_{20}H_{24}OS$: C, 76.88; H, 7.70; S, 10.26. Found: C, 76.90; H, 7.71; S, 10.35.

6,6,6-Trifluoro-3-phenylsulfinyl-2-methyl-5-trifluoromethyl-1,3,4-hexatriene (**3c**).

Following the general procedure for vinylsulfoxyallene preparation, 0.63 g (87% in THF, 2.35 mmoles) of 1,1,1-trifluoro-5-methyl-2-trifluoromethyl-5-hexen-3-yn-2-ol (**2c**), 0.52 g (2.35 mmoles) of benzenesulfenyl chloride, and 0.5 ml of triethylamine afforded a crude product mixture, which was chromatographed on a silica gel column (with a 80% hexane, 20% ethyl acetate, (v:v)) to give 0.51 g (64%) of 6,6,6-trifluoro-3-phenylsulfinyl-2-methyl-5-trifluoromethyl-1,3,4-hexatriene (a colorless oil); ir (neat): 3062, 1956, 1384, 1312, 1181, 957 and 704 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.85 (s, 3H), 5.48 (s, 1H), 5.79 (s, 1H), 7.54-7.58 (m, 3H) and 7.66-7.70 (m, 2H); ^{13}C-nmr (deuteriochloroform): δ 22.2, 102.3 (q, J = 38 Hz), 119.9 (q, J = 274 Hz), 120.9, 125.0, 129.0 (q, J = 225 Hz), 129.4, 131.8, 132.6, 136.5, 141.0 and 200.7.

Anal. Calcd. for $C_{14}H_{10}F_6OS$: C, 49.42; H, 2.96. Found: C, 50.02; H, 3.18.

General Procedure for MTAD Cycloadditions.

An oven-dried, three-necked, round-bottomed flask equipped with a pressure-equalizing dropping funnel (or a calibrated syringe) was charged with a solution of the appropriate vinylallene in methylene chloride. This solution was cooled to −77° and then a solution of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) (1 equivalent) in methylene chloride was added dropwise. Stirring was continued at −77° for 10 minutes and the bath was allowed to slowly warm to room temperature. The reaction mixture was rotary evaporated to remove the solvents and the residue was chromatographed on a silica gel column to give the cycloadduct.

Cycloaddition of **3a** with MTAD.

Compound **3a** (68 mg, 0.26 mmole) and 30 mg (0.26 mmole) of MTAD afforded a crude product, which was chromatographed on a silica gel column (50% hexane, 50% ethyl acetate (v:v)) and gave 87 mg (90%) of 5-cyclopentylidene-5,8-dihydro-2,7-dimethyl-7-phenylsulfinyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (**4**), colorless oil; ir (neat): 3065, 2954, 2869, 1759, 1702, 1453, 1400, 1268, 1100, 1047, 734 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.6-1.8 (m, 4H), 2.18 (s, 3H), 2.4-2.8 (m, 4H), 2.90 (s, 3H), 4.0-4.1 (m, 2H) and 7.34-7.45 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 24.8, 24.9, 26.9, 32.6, 33.2, 46.6, 115.7, 123.4, 128.9, 130.4, 138.5, 143.0, 144.0, 149.3, 150.5 and 151.6; hrms Calcd. for $C_{19}H_{21}N_3O_3S$: 371.4629. Found: 371.4625.

Cycloaddition of **3b** with MTAD.

Following the general procedure for allene cycloaddition with

MTAD, 180 mg (0.58 mmole) of **3b** and 65 mg (0.58 mmole) of MTAD afforded a crude product mixture, which was chromatographed (80% hexane, 20% ethyl acetate (v:v)) to give 214 mg (87%) of a isomer mixture (30:70) of 5-cyclohexylidene-5,7,8,9,10,-10a-hexahydro-2-methyl-6-phenylsulfinyl-1*H*-[1,2,4]triazolo[1,2-*a*]-cinnoline-1,3(2*H*)-dione (**5**); ir (neat): 2934, 2860, 1758, 1697, 1456, 1237, 1041, 905 and 724 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.0-2.7 (m, 30H, isomer A and B), 2.98 (s, 3H, A), 3.00 (s, 3H), 3.65 (m, 2H, A and B), 3.97 (m, 1H, A), 4.27 (m, 1H) and 7.35-7.47 (m, 10H, A and B); ^{13}C-nmr (deuteriochloroform): δ (isomer A) 25.3, 25.5, 25.6, 27.2, 27.5, 27.8, 31.3, 31.4, 31.7, 32.5, 61.0, 115.0, 123.4, 124.9, 128.7, 128.9, 130.1, 134.5, 145.5, 146.2 and 152.5; hrms Calcd. for $C_{23}H_{27}N_3O_3S$: 425.5551. Found: 425.5553.

Cycloaddition of **3c** with MTAD.

Using the above procedure, 304 mg (0.89 mmole) of **3c** and 101 mg (0.89 mmole) of MTAD gave a crude product mixture, which was chromatographed (80% hexane, 20% ethyl acetate, (v:v)) to give 230 mg (57%) of an isomer mixture of 8-(1-trifluoromethyl-2,2,2-trifluoroethyl)-2,6-dimethyl-7-phenylsulfinyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (**7**) and 8-(1-trifluoromethyl-2,2,2-trifluoroethyl)-5,6-dihydro-2-methyl-6-methylidene-7-phenylsulfinyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (**6**) in a 35:65 ratio.

8-(1-Trifluoromethyl-2,2,2-trifluoroethyl)-2,6-dimethyl-7-phenylsulfinyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (**7**).

This compound was obtained as colorless prisms, mp 155-156°; ir (neat): 2860, 1748, 1443, 1398, 1236, 1157, 909 and 735 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 0.8-2.0 (m, 3H), 2.01 (s, 3H), 3.23 (s, 3H), 6.71 (s, 1H), 7.34-7.40 (m, 2H), 7.43-7.50 (m, 3H); ^{13}C-nmr (deuteriochloroform): δ 13.2, 26.0, 15-35 (m), 91.6, 113.5, 114.8, 114.9, 126.2, 129.2, 131.2, 137.9, 144.3, 144.9.

Anal. Calcd. for $C_{17}H_{13}F_6N_3O_3S$ (453.4): C, 45.04; H, 2.89. Found: C, 45.25; H, 2.91.

8-(1-Trifluoromethyl-2,2,2-trifluoroethyl)-5,6-dihydro-2-methyl-6-methylidene-7-phenylsulfinyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (**6**).

This compound was obtained as colorless prisms, mp 103-105°; ir (neat): 2853, 1804, 1740, 1694, 1490, 1443, 1399, 1233, 1159, 1092, 1010, 910 and 739 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 0.8-2.0 (m, 3H), 3.23 (s, 3H), 4.31 (d, J = 16 Hz, 1H), 4.90 (d, J = 16 Hz, 1H), 5.36 (s, 1H), 5.63 (s, 1H), 7.34-7.50 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 26.0, 20-35 (m), 45.1, 93.9, 115.9, 126.1, 129.3, 131.1, 133.4, 133.5, 137.1, 146.4, 149.4.

Anal. Calcd. for $C_{17}H_{13}F_6N_3O_3S$: C, 45.04; H, 2.89. Found: C, 45.34; H, 2.94.

General Procedure For Singlet Oxygenation of Vinylsulfoxyallenes.

In a 250 ml round bottom flask fitted with a gas inlet and outlet, were placed, under an oxygen atmosphere, a 0.05*M* carbon tetrachloride solution of the appropriate vinylsulfoxyallene and a catalytic amount (*ca.* 3 mg) of tetraphenylporphrin (TPP). The solution was cooled to −15° and was irradiated with 400W sodium lamp. The reaction temperature was maintained between −10° and −15° for the duration of the oxygenation. The reaction progress was monitored *via* ir spectroscopy following the disappearance of the characteristic allene stretching frequency at 1900 cm^{-1}. After 3-4 hours, the vinylsulfoxyallene had been totally consumed. The solvent was then removed under reduced pressure and the crude product was analyzed *via* nmr.

Spiro[cyclopentane-1,6′-[3′]-methyl-5′-oxa-2′-phenylsulfinyl-2′,2-cyclohexeneone] (**9**).

Using the singlet oxygen procedure described above, 450 mg (1.74 mmoles) of **3a** and TPP afforded **9** in 90% yield: ir (neat): 2960, 2874, 1672, 1615, 1445, 1084, 911, 733 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.33-2.30 (m, 8H), 2.18 (s, 3H), 4.21 (s, 1H), 4.23 (s, 1H), 7.31-7.69 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 193.1, 164.1, 143.7, 132.8, 131.5, 128.6, 124.9, 88.9, 66.2, 33.6, 33.2, 24.5, 14.1.

Spiro[cyclohexane-1,4′-[1′]-ene-5′-oxa-3′-oxo-2′-phenylsulfinylbicyclo[4.4.0]decane] (**12**).

Singlet oxygenation of **3b**, 450 mg (1.4 mmoles) afforded **12** in 88% yield; ir (neat): 2937, 1667, 1445, 1147, 746 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.26-2.47 (m, 18H), 3.81 (t, 1H), 7.27-7.63 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 20.5, 21.1, 23.4, 25.1, 26.4, 28.4, 31.2, 35.0, 70.4, 78.0, 123.9, 128.8, 130.0, 132.6, 169.0, 193.8.

General Procedure for Peracid Oxidation of Pyranones **9** and **12**.

In a 250 ml round bottom flask fitted with a magnetic stirrer and dropping funnel, were placed 0.06*M* of a methylene chloride solution of the corresponding pyran. To the stirred solution, maintained at 0°, were slowly added 0.1*M* solution of *meta*-chloroperoxybenzoic acid (MCPBA) in dichloromethane. The mixture was stirred overnight and then washed with 3 x 25 ml of sodium bicarbonate, water, and brine. the organic layer was dried over magnesium sulfate, filtered and the solvent evaporated to give a crude product which was purified by silica gel chromatography (80% hexane, 20% ethyl acetate (v:v)).

Spiro[cyclopentane-1,6′-[3′]-methyl-5′-oxa-2′-phenylsulfonyl-2′,2-cyclohexenone] (**10**).

Pyran **9** (860 mg, 2.9 mmoles) and 840 mg (2.9 mmoles) of MCPBA gave **10** in 50% yield (a pale yellow oil); ir (neat): 2954, 1680, 1595, 1438, 1147, 990 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.64-1.83 (m, 8H), 2.47 (s, 3H), 4.41 (s, 2H), 7.48-8.01 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 190.9, 167.3, 141.6, 133.2, 128.5, 128.3, 127.9, 88.8, 66.5, 34.0, 24.4, 17.0.

Anal. Calcd. for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92; S, 10.46. Found: C, 62.91; H, 5.87; S, 10.32.

Spiro[cyclohexane-1,4′-[1′]-ene-5′-oxa-3′-oxo-2′-phenylsulfonylbicyclo[4.4.0]decane] (**13**).

Compound **12** (800 mg, 2.3 mmoles) and 700 mg (2.3 mmoles) of MCPBA afforded **13** in 49% yield (a white solid), mp 118.5-120°; ir (neat): 2940, 2867, 1692, 1586, 1448, 1308, 1153, 649 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.15-2.06 (m, 17H), 2.31 (m, 1H), 4.28 (m, 1H, isomer A), 4.51 (m, 1H, isomer B), 7.48-7.97 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 20.6, 21.1, 23.7, 25.0, 27.0, 28.2, 28.6, 31.6, 35.8, 71.3, 77.9, 127.8, 128.5, 130.8, 133.0, 141.8, 172.1, 192.0.

Anal. Calcd. for $C_{20}H_{24}SO_4$: C, 66.64; H, 6.71; S, 8.89. Found: C, 66.35; H, 6.67; S, 8.73.

Spiro[cyclopentane-1,4′-[1′]-methyl-3′,7′-dioxa-5′-oxo-6′-phenylsulfinylbicyclo[4.1.0]heptane] (**11**).

In a 100 ml round bottom flask fitted with a magnetic stirrer and dropping funnel, were placed 290 ml (1.0 mmole) of **9** and 1 ml (1.4 mmoles) of hydrogen peroxide (30%) in 10 ml of dichloro-

methane. The reaction flask was cooled to 15°, after which a solution of 0.5 ml (3.0 mmoles) of 6*N* aqueous sodium hydroxide was added dropwise with stirring over a period of one hour. During the addition, the temperature of the reaction mixture was maintained at 15-20°. The organic layer was then treated with 5% sodium bicarbonate, water and then brine. The organic layer dried over magnesium sulfate and the solvent was evaporated to give after chromatography (4:1 hexanes/ethyl acetate) epoxide **11** in 65% yield (a white solid), mp 171-172°; ir (neat): 2911, 1702, 1438, 1090, 748 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.54-1.81 (m, 8H), 1.86 (s, 3H), 3.84 (s, 2H), 7.48-7.88 (m, 5H); ^{13}C-nmr (deuteriochloroform): δ 12.3, 24.6, 24.7, 34.9, 38.5, 63.8, 70.4, 76.3, 91.8, 126.5, 128.8, 131.6, 141.4, 206.3.

Anal. Calcd. for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92; S, 10.46. Found: C, 62.87; H, 5.93; S, 10.34.

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