value for an aromatic hydrocarbon and is close to that reported[14] for *trans*-stilbene, 3.9×10^7 s^{-1}. An approximate value of $\phi_{\rm is}$ at various temperatures or for other alkyl-substituted styrenes can probably be obtained by using the value $k_{\rm is} = 3 \times 10^7$ s^{-1} and the fluorescence lifetime of the compound considered at the temperature of interest.

Acknowledgment. We thank Professor Mattler and Dr. Kopec, from the "Université de Paris VI", who lent to us the He–Cd laser used in this work, and Professor Joussot-Dubien for stimulating discussions and encouragement.

Registry No. PhCH=CH$_2$, 100-42-5; PhCH=CH(C$_2$H$_5$), 824-90-8; PhC(CH$_3$)=CH(C$_2$H$_5$), 53172-84-2; PC6, 771-98-2; PN, 4237-08-5.

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[14] Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York 1980; Vol. 3, p 46.

Preparation and Reactions of 1-(Phenylthio)-2-[(trimethylsilyl)oxy]-1,3-butadienes. A One-Pot Synthesis of Sulfur-Substituted 7-Hydroxybicyclo[2.2.1]heptanones: Coupling of the Diels-Alder Reaction with the Aldol Process

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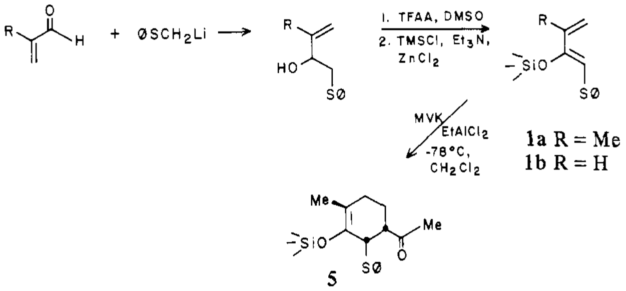
Received January 14, 1982

In the midst of our studies directed toward the total synthesis of the rubradirins,[2] we had the occasion to prepare and to examine the properties of the new diene **1a**. This compound was produced in acceptable overall yield from the alcohol formed on addition of lithiated thioanisole to methacrolein.[3] The oxidation state of this alcohol was taken to the ketone level by use of the Swern procedure, and the resulting 3-methyl-1-(phenylthio)-3-buten-2-one was trimethylsilylated with TMSCl/Et$_3$N/ZnCl$_2$[4] to produce stereospecifically (*Z*)-3-methyl-1-(phenylthio)-2-[(trimethylsilyl)oxy]-1,3-butadiene (**1a**).



5

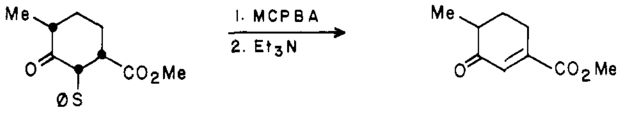
Room-temperature Diels–Alder reaction of this new diene with maleic anhydride proceeded well as long as the reaction mixture was concealed from light or contained a small amount of diphenyl disulfide.[5] ^{1}H NMR decoupling experiments on the crystalline cycloadduct **2** established that the reaction had proceeded in the expected endo fashion and did furthermore substantiate the Z nature of the starting diene.

While the room-temperature reaction of **1a** with *N*-phenylmaleimide also proceeded well to give the crystalline adduct **3** (Table I), less reactive dienophiles failed to give clean reaction products. Consequently, the reactions of **1a** were examined in the presence of Lewis acids. With *p*-benzoquinone and zinc chloride as catalyst, [4 + 2] cycloaddition gave a crude adduct that was cleaved immediately with hydrofluoric acid in acetonitrile to the crystalline ketone **4**. Use of 300-MHz ^{1}H decoupling experiments established the stereochemistry depicted in this structure, thus signifying that protonation of the enol silyl ether had taken place on the convex face of the molecule.

For the even less reactive dienophiles such as methyl vinyl ketone and methyl acrylate, ethylaluminum dichloride was employed as catalyst. The EtAlCl$_2$-catalyzed reaction of diene **1a** with MVK was complete within 20 min at −78 °C in methylene chloride solvent. A quantitative yield of the endo cycloadduct **5** was obtained. As indicated by the criteria of TLC and 300-MHz ^{1}H NMR analysis, the product was a single isomer of high purity.

Hydrofluoric acid assisted cleavage of the enol silyl ether **5** gave two products in a ratio of 5.5:1 whose structures were identified tentatively through 300-MHz ^{1}H NMR decoupling experiments to be compounds **6** and **7**, respectively. Protonation in this case presumably occurs predominately opposite the pseudoaxial phenylthio substituent.

The ethylaluminum dichloride catalyzed reaction of **1a** with methyl acrylate took place at 0 °C to afford a cycloadduct in 90% crude yield. On silyl ether cleavage, a 1.4:1 mixture of (carbomethoxy)cyclohexanones **8** and **9** was generated in 66% isolated yield. Oxidation of phenylthio group of **8** with MCPBA yielded a sulfoxide which underwent elimination in the presence of triethylamine to give the cyclohexenone **10** in 80% yield, a compound that should itself function as a useful Diels–Alder dienophile.



8 10

Of all the reactions we studied with diene **1a**, the α,β-unsaturated aldehydes were found to react in the most startling manner. The EtAlCl$_2$-catalyzed reaction of **1a** with methacrolein was complete within 15 min at −78 °C in methylene chloride as solvent. After a bicarbonate workup and hydrolysis with 5% HCl in acetone to remove the silyl group, a light yellow oil was obtained in 90% yield upon column chromatography. The ^{1}H NMR of this new product showed *no* aldehydic (C(O)*H*) proton. Instead, two sharp methyl singlets and a broad peak at δ 3.73 were found. The IR spectrum revealed a broad absorption at 3420 cm^{-1}. After careful deliberation, it was realized that the Diels–Alder reaction had indeed taken place but that this had been accompanied by a Mukaiyama-like intramolecular aldol condensation[6] to produce **11** on silyl ether cleavage. Europium shift studies indicated that the sterochemistry of the bicyclic was as indicated in the table with the hydroxy group syn to the sulfur substituent, for the H$_{5e}$ and H$_{6e}$ protons moved downfield to almost the same degree as did the H$_{3n}$ proton on addition of increasing amounts of the shift reagent.[7] Mechanistically, this stereochemical result suggests that after the Diels–Alder reaction, the aluminum catalyst may coordinate to both the aldehyde carbonyl and the phenylthio substituent of the cycloadduct to give the six-membered chelate structure **13**, which now undergoes the internal aldol reaction with

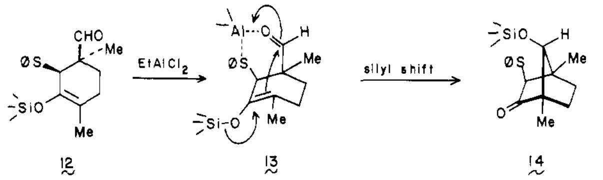


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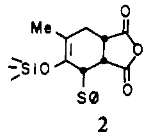
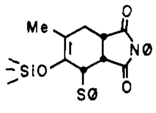
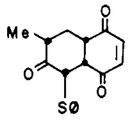
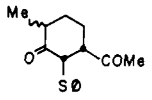
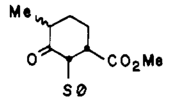
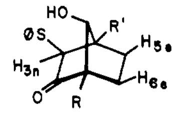
Table I. Diels-Alder Reactions of 1-(Phenylthio)-2-(trimethylsilyl)oxy-1,3-butadienes **1a** and **1b**

dienophile	diene	reaction conditions[b]	product	isolated yield, %
maleic anhydride	1a	4d, rt,[a] CH_2Cl_2	 **2**	65
N-phenylmaleimide	1a	3d, rt, CH_2Cl_2	 **3**	48
p-benzoquinone	1a	1.4 h, rt, CH_2Cl_2, $ZnCl_2$, then HF, CH_3CN	 **4**	45
methyl vinyl ketone	1a	20 min, −78 °C, CH_2Cl_2, $EtAlCl_2$, then HF, CH_3CN	 **6**, α-Me; **7**, β-Me	85
methyl acrylate	1a	3 h, 0 °C, CH_2Cl_2, $EtAlCl_2$, then HF, CH_3CN	 **8**, α-Me; **9**, β-Me	66
methacrolein	1a	15 min, −78 °C, CH_2Cl_2, $EtAlCl_2$, then 5% HCl, acetone	 **11, 15-17** **11**, R = R' = Me	90
acrolein	1a	10 min[b]	**15**, R = Me; R' = H	93
methacrolein	1b	4 h[b]	**16**, R = H; R' = Me	88
acrolein	1b	2.5 h[b]	**17**, R = R' = H	11

[a] rt = room temperature. [b] Other conditions as in the reaction of methacrolein with **1a**.

subsequent silyl transfer to afford **14**. In the absence of such chelation, it would seem that formation of the anti alcohol would be preferred on the basis of simple steric considerations.[8]

Diene **1a** also reacted with acrolein at −78 °C in the presence of $EtAlCl_2$ in less than 20 min to yield bicycloheptanone **15** in 93% yield after hydrolysis with 5% HCl in acetone. Product stereochemistry is assigned in analogy to the previous example.

To further examine the scope of this unique route to bicyclics, we prepared the second new diene **1b**.[9] The $EtAlCl_2$ catalyzed reaction of diene **1b** with methacrolein occurred in about 4 h at −78 °C in methylene chloride solvent to provide bicycloheptanone **16** in 88% yield after acid hydrolysis. With acrolein as the dienophile, the isolated yield of **17** was a disappointing but unoptimized 11%. Polymerization may be competitive with cycloaddition in this instance.

The silyoxy-sulfur-substituted dienes do appear to offer an extremely facile, one-pot method for preparing 7-hydroxylated bicyclo[2.2.1]heptane derivatives.[10] We further suggest that such adducts may find use in the generation of highly functionalized cyclopentanes, for Trost has demonstrated that β-keto sulfides can be converted to ring-cleaved diacids on exposure to basic hydrogen peroxide.[11,12]

Acknowledgment. We are indebted to the National Institutes of Health (AI-16138) and the Camille and Henry Dreyfus Foundation for support of this work. The 300-MHz ^1H NMR spectrometer used in these studies was funded by the National Science Foundation (CHE-79-05-185).

Registry No. 1a, 81389-34-6; **1b**, 81389-35-7; **2**, 81389-36-8; **3**, 81027-67-0; **4**, 81389-37-9; **5**, 81389-38-0; **6**, 81389-39-1; **7**, 81389-40-4; **8**, 81389-41-5; **9**, 81389-42-6; **10**, 81389-43-7; **11**, 81389-44-8; **12**, 81389-45-9; **14**, 81389-46-0; **15**, 81389-47-1; **16**, 81389-48-2; **17**,

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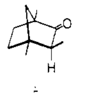
[8] The titanium tetrachloride catalyzed reaction of methacrolein and 2,3-dimethylbutadiene affords bicycloheptanone i by a scheme involving



i

Diels–Alder cycloaddition, intramolecular condensation, Wagner–Meerwein rearrangement, hydride shift, and epimerization. Other examples have been generated. See: Baldwin, J. E.; Lusch, M. *J. Org. Chem.* **1979**, *44*, 1923. Dworan, E.; Buchbauer, G. *Chem. Ber.* **1981**, *114*, 2357. This process, while related to our own, does provide a less functionalized and hence a less versatile bicyclic.

[9] Both dienes **1a** and **1b** were stored as stock solutions in methylene chloride in the dark at 2 °C. A small amount of the radical inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide was also added to these solutions.

[10] For a recent report on the preparation of 7-functionalized norbornenes, see: Fleming, I.; Michael, J. P. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1549.

[11] Trost, B. M.; Massiot, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4405.

[12] Additionally, the bicycles available from such methodology might well be suitable for the synthesis of verrucarol and its analogues. See, for example: Roush, W. R.; D'Ambra, T. E. *J. Org. Chem.* **1981**, *46*, 5045.

81389-49-3; PhSCH$_2$Li, 13307-75-0; H$_2$C=CMeCHO, 78-85-3; H$_2$C=CMeCH(OH)CH$_2$SPh, 81306-15-2; PhSCH$_2$COCMe=CH$_2$, 77004-05-8; maleic anhyride, 108-31-6; *N*-phenylmaleimide, 941-69-5; *p*-benzoquinone, 106-51-4; methyl vinyl ketone, 78-94-4; methyl acrylate, 96-33-3; acrolein, 107-02-8.

Plasma-Exposed Reduction of Solid and Solvated Viologens[†]

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Received November 11, 1981

Considerable attention has been focused on the study of organic radicals prepared by one-electron reduction of the parent molecules, among which viologens (4,4′-bipyridinium salts) have special interests in terms of the photochemical production of hydrogen gas from water.[1-4] We report here that solid and solvated samples of viologens can be reduced exclusively and quickly and can form cation radicals when exposed to a radio-frequency plasma.

The technique of most interest to plasma chemistry is the glow discharge, in which free electrons gain energy from an imposed electrical field and subsequently lose it through collisions with neutral molecules in the gas. The transfer of energy to the gas molecule leads to the formation of a host of chemically active species such as electrons and ions, some of which become precursors to the chemical reactions[5-7] and polymerizations[8,9] as well. It was, therefore, of interest as to whether the energetic electrons in the gaseous plasma could directly induce the reduction of viologens.

The plasma exposure was carried out in an optical quartz cell of 10-mm path length, in which 3 mL of DMF solution of viologen was placed (Figure 1). The cell was inserted between a pair of parallel-plate electrodes connected to an RFG-200 radio-frequency generator, operating at 13.56 MHz and delivering up to 200 W. The solution was frozen, followed by degassing several times at 10^{-4} torr. A glow discharge was then generated in the gas space above the solution for a prescribed period of time according to the method described previously.[10-13]

The transparent DMF solution of benzylviologen (1,1′-dibenzyl-4,4′-bipyridinium dichloride, BV^{2+}) changed to deep blue color as soon as the plasma was exposed. Figure 2 shows the absorption spectra of plasma-exposed BV^{2+} in DMF at various plasma durations measured in vacuo. The spectra were in good agreement with the reported spectra of photochemically reduced viologens,[3,4] showing the monotonous increase of the intensity with the plasma duration. The characteristic absorptions at 402 and 607 nm clearly show the formation of the cation radical, BV$^{+\cdot}$.

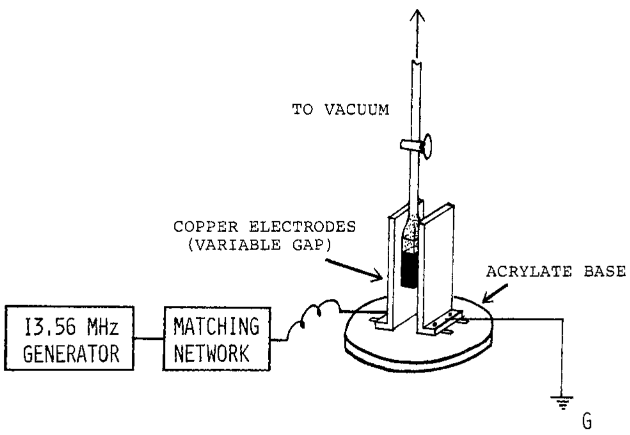


Figure 1. Apparatus for plasma exposure of the viologen solution.

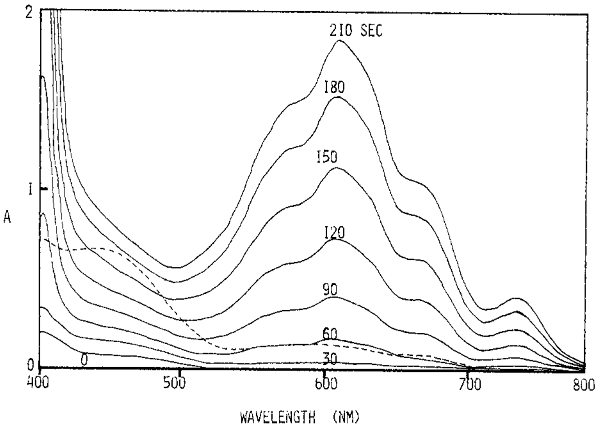
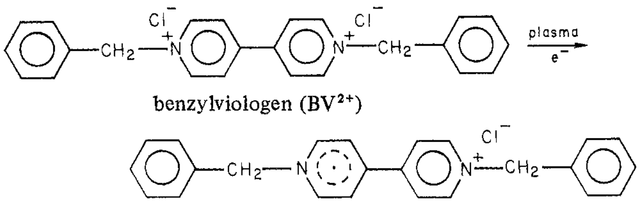


Figure 2. Progressive spectral changes of benzylviologen with plasma duration (spectra were measured after 5 min of plasma exposure). Figures denote plasma duration: after air quenching (---); benzylviologen, 4.88 × 10^{-4} M in DMF (plasma, 100 W).

The spectrum disappeared on exposure to air but reappeared with repeated plasma exposure. This fact suggests that the reduction occurred via a one-electron process:



benzylviologen (BV^{2+})

cation radical of benzylviologen (BV$^{+\cdot}$)

BV$^{+\cdot}$ is the major product, since no spectral absorption other than by BV^{2+} and BV$^{+\cdot}$ appeared in the UV and visible wavelength range. Also, no insoluble product was formed. Furthermore, the efficiency of the reduction was almost the same when BV^{2+} was present during the plasma exposure as when it was added later. The yield of BV$^{+\cdot}$ based on the amount of BV^{2+} was determined from the ESR spectrum by using 2,2-diphenyl-1-picrylhydrazyl and was calculated as 66% for 4.9 × 10^{-4} mol/L of DMF solution by the plasma exposure for 180 s at 100 W. These facts indicate that the reduction of BV^{2+} is the main pathway.

From experiments at different concentrations of BV^{2+} and different plasma powers, the rate of reduction of BV^{2+} can be expressed as follows (Figure 3):

$$d[\mathrm{BV}^{+\cdot}]/dt = K[\mathrm{BV}^{2+}]^{0.5}[\mathrm{power}]^{1.0}$$

where *K* is a constant depending on the plasma reactor.

In addition to the DMF solution of BV^{2+}, a solid sample of BV^{2+} and poly(xylylviologen dichloride) were reduced successfully by the plasma, but no reduction occurred for dichlorides and di-

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[†] Study of Plasma-Initiated Polymerization. 6.

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