to the corresponding sulfoxide (THTO) by *tert*-butyl hydroperoxide (TBHP). The catalytic effect in this case (70 °C in CH_3CN): $k_{\text{catalyzed by }1}/k_{\text{uncatalyzed}} = 27$.

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Supplementary Material Available: Tables of crystal data, atom coordinates, temperature factors, and bond lengths and angles for $(n\text{-}Bu_4N)_3V_{13}O_{34}$ (20 pages); table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Photochemical Generation and Preparative Capture of 1,2,4,5-Tetramethylenebenzene in Fluid Solution. Nanosecond Time-Resolved Spectroscopic Determination of Absolute Rates of Dimerization and Oxygen Trapping of a Disjoint Singlet Hydrocarbon Biradical

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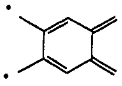
A single species, assigned as 1,2,4,5-tetramethylenebenzene (TMB, **1**), is responsible for both the CP MAS ^{13}C NMR spectrum and the UV–vis (λ_{max} = 490, 570, and 625 nm, $\epsilon \approx 4200$, 600, and 400, respectively) spectrum of matrix-immobilized preparations obtained by irradiation of the ketone **2** at 77 K.[2] The ESR spectrum observed[2,3a] under these conditions is associated with a different carrier.[2] An alternative to **1** as the carrier of the NMR signal, the bicyclic hydrocarbon **3**, was considered to be less satisfactory.[2] These data led to the assignment of a singlet spin state to the biradical **1**.[2] In contrast, the reported[3b,c] "multiplicity-specific" behavior of **1** (O_2 gives peroxides, but alkenes do not react) is interpreted[3b] as consistent with the earlier assignment[3a] of a triplet spin state of **1**.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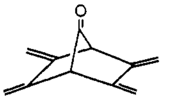
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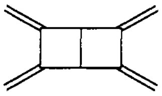
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We now find the capture of **1** not to be multiplicity-specific, since photochemically generated **1**, like other singlet biradicals such as 3,4-dimethylenefuran and 3,4-dimethylenethiophene,[4,5] combines readily in preparative reactions with singlet *or* triplet reagents. For example, photolysis of ketone **2** (0.03 M in $CHCl_3$ solution) in the presence of maleic anhydride (MA, 0.5–1.0 M, Rayonet reactor, 300 nm, 0 °C) leads to the formation of a 2:1 MA:**1** adduct (78% isolated yield). The rate of disappearance of **2** is independent of the concentration of the alkene. Under these conditions, the thermal Diels–Alder reaction of **2**,[2,6] which also could give the same adduct, does not occur. Similar preparative experiments with oxygen-saturated samples of **2** give the bridged monoperoxide and fused diperoxide of **1** in 30% and 55% yields, respectively.

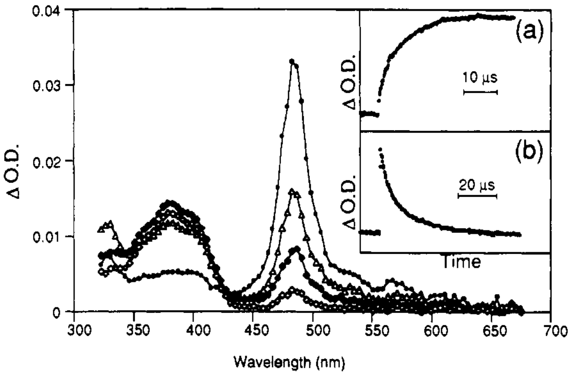

Figure 1. Transient absorption spectra of the biradical 1,2,4,5-tetramethylenebenzene (**1**) generated by 308-nm laser flash photolysis of ketone **2** in $CHCl_3$ at 291 K: 0.3 (●), 7.0 (△), 16.6 (◆), and 33.2 (◇) μs after laser flash. Insets: (a) growth kinetics measured at 380 nm; (b) decay kinetics measured at 490 nm.

Nanosecond laser flash photolysis experiments[7] now have afforded direct measurements of the kinetics of TMB reactions. Deoxygenated samples of **2** in $CHCl_3$, toluene, or CH_3CN in a 7 × 7 mm flow cell (initial optical densities ~0.3 at 308 nm) were subjected to 308-nm laser pulses. Transient spectra (see Figure 1) with maxima corresponding to those observed[2,3a] in the matrix-immobilized experiments were acquired by recording delay traces at various wavelengths. The pulses typically produced initial transient concentrations of $\sim 1 \times 10^{-5}$ M. The decay of the transient absorption as a function of time was monitored by a photomultiplier-transient digitizer system.

The disappearance of the 490-nm absorption could be fitted to second-order (but not first-order) kinetics, with rate constants ($2k_t$ in $M^{-1}\ s^{-1}$, based on $\epsilon_{490} = 4200\ M^{-1}\ cm^{-1}$) for dimerization of 2.1×10^{10} ($CHCl_3$), 1.5×10^{10} (toluene), and 3.0×10^{10} (CH_3CN). The bands at 570 and 625 nm disappeared at the same rate as the 490-nm band, which indicates that all three bands share the same carrier. The probable uncertainty in the rate constants is about 50%, primarily because of the uncertainty of ~25% in the extinction coefficient of the biradical. The dimerization rates, like that of 3,4-dimethylenefuran ($3.3 \times 10^{10}\ M^{-1}\ s^{-1}$ in CH_3CN),[4a,b] are near the encounter-controlled limit calculated for singlet biradicals without spin-statistical correction.

The decay of the 490-nm transient was accompanied by the appearance (Figure 1) of a new species with an absorption maximum at about 380 nm, characteristic[8] of *o*-quinodimethane units. Similar absorption peaks (and emission and excitation spectra) concordant with *o*-quinodimethane were observed in matrix preparations of **2** which had been irradiated, annealed, and refrozen. In the solution-phase flash experiments, the growth at 380 nm initially followed the same kinetic order as the decay at 490 nm, and the absorption profile was similar to that observed for the 380-nm chromophore in the matrix experiments. The subsequent polymerization of the dimer(s) was slow on the nanosecond time scale but was observable as a slight decrease in the 380-nm absorption after several microseconds (33.2-μs curve, Figure 1).

Under the laser flash conditions, the 490-nm transient was quenched by oxygen with pseudo-first-order kinetics in either oxygen-saturated or air-saturated $CHCl_3$, from which we derived

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a rate constant of 1.9×10^7 M^{-1} s^{-1} at 291 K. This rate for the solution-phase reaction, which is only $\sim 10^{-3}$ of the encounter rate, may be spin-restricted, but in any case, it suggests that the assumption[3b] of a collision-controlled rate for the gas-phase **1** + O_2 reaction may be in error by a similar factor. If so, the corrected rate for the gas-phase reaction in turn would require revision of the derived[3b] heat of formation of **1**.

Attempts to quench the flash photolytically produced 490-nm transient with conventional dienophiles (diethyl fumarate, maleic anhydride, fumaronitrile) were unsuccessful. This places an upper limit of $\sim 10^4$ M^{-1} s^{-1} for the reaction rate of **1** with these traps. This slow rate of reaction with alkenes is not surprising; frontier MO considerations predict that **1** should be less reactive toward electron-poor dienophiles than the electron-rich biradicals 3,4-dimethylenefuran and 3,4-dimethylenethiophene, which are quenched by such reagents under flash photolytic conditions.[4a,b]

The factor of $\geq 10^6$ by which the dimerization rate of **1** exceeds that[9] of the closed-shell molecule *o*-quinodimethane is a dramatic consequence of non-Kekulé character in **1**. Dimerization rates in the 10^{10} s^{-1} range are not expected for the hypothetical alternative bicyclic structure **3**. The hypothesis that photolysis of **2** gives rise mainly (95%) to the bicyclic hydrocarbon **3** and a small amount (5%) of **1**, previously discounted[2] on other grounds, is also refuted by the absolute rates observed here, since the rate constant deduced from a hypothetical 20-fold increased extinction coefficient for **1** would have to be 400 times the encounter-limited maximum rate.

The absolute rate measurements thus help to exclude **3** and confirm the previous assignment[2] of biradical **1** as the carrier of the observed CP MAS ^{13}C NMR and UV–vis spectra. Our present and previous[2] findings are consistent with the theoretical predictions[10] of a singlet state for this disjoint species.

Acknowledgment. We thank the United States National Science Foundation for a grant in support of this research.

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Thiophene–Silole Cooligomers and Copolymers

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Polythiophenes, as well as other π-conjugated polymers, have received considerable attention in research on conducting polymers and molecular electronics.[1] Current interest has especially been directed toward structure modifications, including side chain introduction for solubility improvement[2] and for development of new functions,[3] control of the chain lengths,[4] regularity,[5] and geometry,[6] and the synthesis of copolymers and cooligomers with other conjugated ring systems in the main chain.[7]

Scheme I

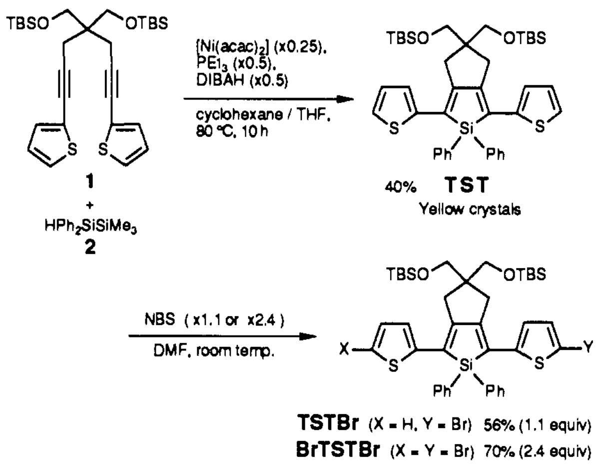
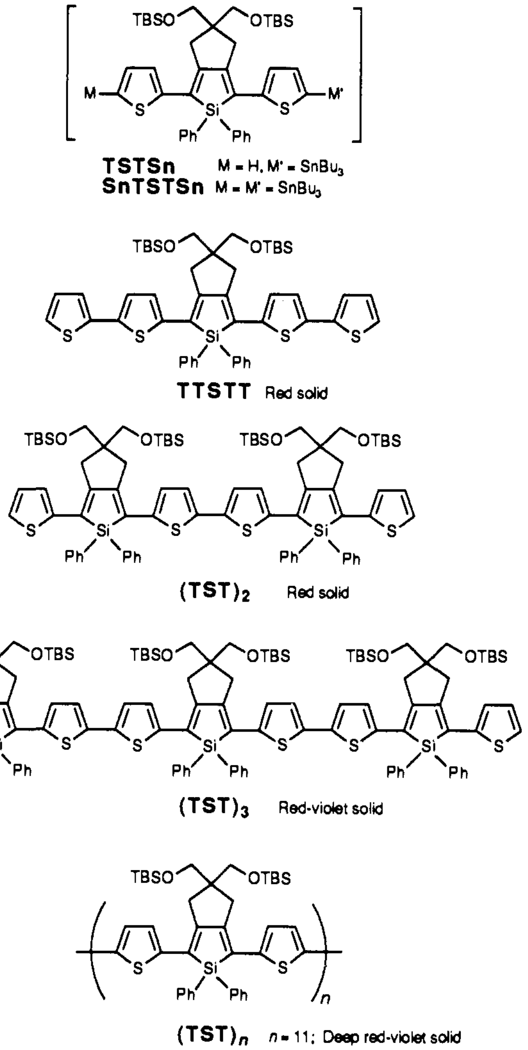


Chart I



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