heating the mixture at 80–90 °C for 6 h gave, after protonolysis, a 68% yield of **14g**.

Finally, the reaction of $Cp_2Zr(CH_2CH_2Ph)_2$ generated in situ with styrene (1.1 equiv) in THF at −78 to 0 °C displayed yet another, albeit predictable, regioselectivity pattern. The ^1H NMR spectrum of the zirconacyclic product (**19**) showed a dominant singlet at δ 5.85 ppm. Protonolysis with anhydrous HCl in ether at −78 °C provided a 90:10 mixture of 1,4- and 1,3-diphenylbutanes in 70% isolated yield (80% by GLC), while its carbonylation followed by protonolysis with anhydrous HCl in ether at −78 °C afforded *trans*-2,5-diphenylcyclopentanol (**20**) in 45% yield along with minor amounts of unidentified but apparently isomeric products.

The results presented above expand the synthetic utility of the rapidly growing methodology involving 3- and 5-membered zirconocene and hafnocene derivatives.[2,4,7–11]

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An Estimate of the Lifetime of 1,4-Dioxybutane Biradicals

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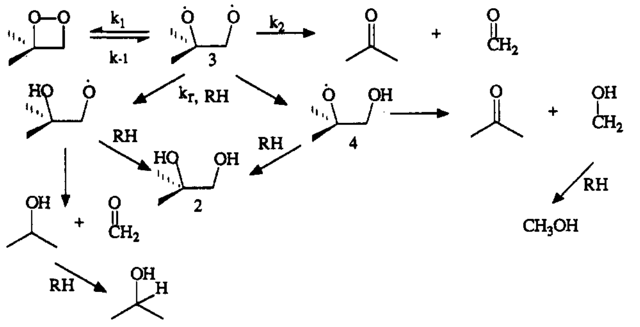
Summary: Previous kinetic data for the thermolysis of 1,2-dioxetanes has suggested a biradical or biradicaloid decomposition route, but direct evidence for a biradical intermediate has been lacking. We now report the trapping of a 1,4-dioxybutane biradical in the thermolysis of 3,3-dimethyl-1,2-dioxetane, where the lifetime is estimated to be in the range of 30–75 ps. Attempts to trap biradicals from the thermolysis of trimethyl- and tetramethyl-1,2-dioxetane were unsuccessful, and it was estimated that the maximum lifetimes of these biradicals were 7 ps.

Sir: There has been a growing interest in biradicals and their detection as intermediates in chemical and photochemical reactions.[1] Considerable evidence has been presented for 1,4-butane biradicals that are produced in the Norrish Type II photolysis of ketones.[2] The 1,4-butane biradical has also been postulated as intermediate in the thermal decomposition of cyclobutanes, based on kinetics[3] and the cis/trans isomerization of substituted cyclobutanes.[4] In the thermolysis of 1,2-dioxetanes, a stepwise mechanism has been proposed where 1,4-dioxybutane biradicals are postulated intermediates.[5] However, it has also been suggested that dioxetanes undergo ther-

Scheme I



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molysis in a concerted fashion with biradical character in the transition state.[6] As yet, direct evidence for biradical intermediates in the thermolysis of dioxetanes has not been reported. From trapping experiments with a H-atom donor, we now report evidence for the 1,4-dioxybutane biradical intermediate in the thermolysis of 3,3-dimethyl-1,2-dioxetane (1).

Thermolysis of some simple methyl-substituted dioxetanes in the presence of 1,4-cyclohexadiene as hydrogen atom donor was studied. 1,4-Cyclohexadiene was selected as an oxy-radical trap, since it is among the best of the hydrogen atom donors,[7] and it should not enter into redox reactions with the dioxetanes as would donors such as mercaptans.[8] Possible reactions and products in the thermolysis of 3,3-dimethyl-1,2-dioxetane (1) with a hydrogen atom donor are shown in Scheme I. In this example, acetone and formaldehyde are the normal products that are formed in the absence of an excellent hydrogen atom donor solvent. In the presence of such a solvent, for example 1,4-cyclohexadiene, *possible* trapping products of biradical 3 are 2-methyl-1,2-propanediol (2), isopropyl alcohol, and methanol. When dioxetane 1 (0.00379–0.0758 M) was decomposed at 50.0 °C for 5.0 h (ca. 10 half-lives) in aerated 1,4-cyclohexadiene as the solvent (10.6 M), acetone and glycol 2 were the only products observed by GC analysis. The formation of glycol 2 was confirmed by MS/GC analysis. Peaks were not detected at the glycol 2 retention time when dioxetane was omitted or when dioxetane 1 (0.0379 M) was decomposed in benzene under the same conditions. In the latter case, a 99% yield of acetone was observed.

Since glycol 2 could be formed as shown in Scheme I or by induced decomposition of the dioxetane, the initial concentration of dioxetane was varied in order to distinguish these processes. The yields of glycol 2 at various initial dioxetane concentrations are given for decompositions in 1,4-cyclohexadiene solvent at 50 °C for 5.0 h: 9.85% (0.00379 M), 10.8% (0.0152 M), 14.4% (0.0303 M), 13.7% (0.0379 M), 17.7% (0.0531 M), and 18.2% (0.0758 M). A plot of these data, with a least-squares fit line, is shown in Figure 1. Even with a consideration for error in the intercept, it is clear that glycol 2 is produced as the dioxetane concentration approaches zero and thus where *no* bimolecular induced decomposition occurs. The 9.6% yield of 2, obtained by extrapolating to zero dioxetane concentration, represents the yield of glycol associated with the unimolecular decomposition of the dioxetane. Since it was shown that glycol 2 is *not* formed in the absence of the 1,4-cyclohexadiene hydrogen atom donor, trapping of the biradical 3 as shown in Scheme I is the most reasonable explanation for the generation of 2 as dioxetane concentration approaches zero.

From the yield of glycol 2 and acetone, along with a value for H-atom abstraction from 1,4-cyclohexadiene by *tert*-butoxy radicals,[9] the lifetime of biradical 3 ($\tau = 1/k_2$) can be calculated with the aid of eq 1 and 2. The v's are rates, [RH] is cyclohexadiene concentration (10.6 M), and k_r (1.36×10^8 s^{-1} at 50.0 °C) is twice the value for H-atom abstraction from 1,4-cyclohexadiene by *tert*-butoxy radical.

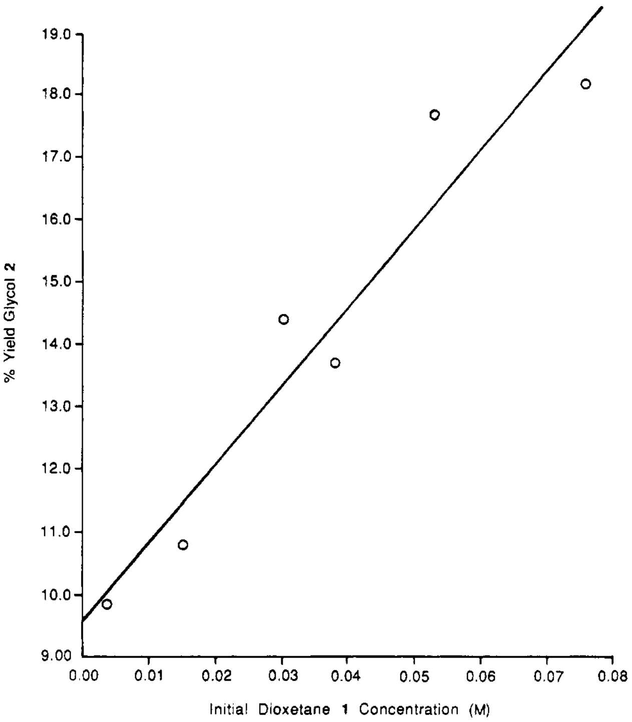

Figure 1. Percent yield of glycol 2 vs initial concentration of dioxetane 1, where the least-squares equation is: % yield glycol 2 = (126 ± 19)[dioxetane 1]$_0$ + (9.55 ± 0.82), $r = 0.958$, $S_{y,x} = \pm 1.1\%$ yield glycol 2.

$$v(\text{acetone})/v(\text{glycol}) = \frac{(\%\text{ yield acetone})}{(\%\text{ yield glycol})} = \frac{k_2[\mathbf{3}]}{k_r[\mathbf{3}][\mathrm{RH}]} \tag{1}$$

$$k_2 = \frac{k_r(\%\text{ yield acetone})[\mathrm{RH}]}{(\%\text{ yield glycol})} \tag{2}$$

With these data, the lifetime of the biradical 3 is calculated to be 75 ps. Calculation of τ by eq 2 assumes that acetone is not produced from radical 4. This is a reasonable assumption, since the companion product methanol in this possible reaction is not observed. This estimate of the lifetime of biradical 3 assumes that the *tert*-butoxy radical serves as a good model for the rate of hydrogen atom abstraction from either the tertiary or primary alkoxy radical site in 3. In fact, the rate of hydrogen atom abstraction by tertiary alkoxy radicals is reported to be 2- to 4-fold slower than primary alkoxy radicals at 27 °C.[10] If an account is made for this difference between rates of tertiary and primary alkoxy radicals, the estimated lifetime of biradical 3 is decreased to 30–50 ps.

Similar trapping experiments were performed with trimethyl- and tetramethyl-1,2-dioxetane in 1,4-cyclohexadiene solvent. In neither instance was the corresponding glycol detected by GC analysis.[11] At the highest dioxetane concentration (0.04 M), we estimate that a 1% yield of glycol could be detected, but this is at our de-

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tectability limits. If it is assumed that 1% or less yield of glycol could be undetected at 0.04 M dioxetane concentration, then the *maximum* lifetime of the biradicals derived from trimethyl- and tetramethyl-1,2-dioxetane is calculated to be 7 ps from eq 2.

These results show that certain 1,4-dioxy biradicals may be discrete intermediates in the thermolysis of dioxetanes. However, even the more stable of these biradicals are very short lived. With increased methyl substitution, the trimethyl- and tetramethyl-1,4-dioxybutane biradicals cannot be trapped with 1,4-cyclohexadiene, and the lifetime is 7 ps or less. With an estimated vibrational lifetime of 0.1 ps for a 1,4-dioxybutane biradical, based on the C–C stretching frequency, the trimethyl- and tetramethyl-substituted biradicals may or may not be true intermediates. It is interesting to note that the 1,4-dioxybutane biradicals have much shorter lifetimes than the corresponding carbon-centered biradicals. For example, carbon-centered 1,4-diyls produced in photochemical reactions of ketones are estimated to have lifetimes in the microsecond to nanosecond region.[2]

Acknowledgment. We thank Dr. J. C. Scaiano and P. McGarry for determining the absolute rate and activation parameters for H-atom abstraction from 1,4-cyclohexadiene by *tert*-butoxy radical. This work was supported by National Science Foundation Grant CHE-8413738.

Articles

Samarium-Promoted Cyclopropanation of Allylic Alcohols

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The use of samarium/mercury amalgam in conjunction with diiodomethane or chloroiodomethane to generate samarium carbenoids for the efficient cyclopropanation of allylic alcohols is discussed. These hydroxyl-directed cyclopropanations occur under mild conditions and allow a wide range of substitution about both the olefin and the carbinol carbon in allylic alcohol substrates. High yields and high diastereoselectivities are observed for many substrates.

The cyclopropane structural unit is found in many naturally occurring substances and is often incorporated into other synthetically derived compounds of biological interest, including steroid analogues.[2] In addition, diastereoselectively generated cyclopropanes have proven to be useful synthons for further transformation to stereodefined cyclic and acyclic compounds.[3]

The most widely recognized methodology for the stereoselective generation of cyclopropanes is the Simmons–Smith reaction, which has a proven record of service.[4] While the Simmons–Smith cyclopropanation procedure is generally quite effective, it suffers from both harshness and inconvenience due to the inhomogeneity of the reaction mixture and low reactivity of zinc metal. For example, reaction times approaching 60 h in boiling ethyl ether are required in some cases.[4a] Variations of the zinc-promoted Simmons–Smith reaction have been introduced with some success. The Furukawa modification utilizing diethylzinc as a reductant has proven useful in many cases,[5] as has the protocol of Yamamoto, which employs triethylaluminum and diiodomethane.[6] The pyrophoric nature of diethylzinc and triethylaluminum utilized in these procedures renders them somewhat less attractive. Recently, dichlorocarbene reactions have been demonstrated to be highly diastereoselective.[7] However, this strategy and the Seyferth methodology[8] both suffer from the need for subsequent reduction of the halocyclopropanes produced in the reaction in cases where unfunctionalized cyclopropanes are desired. Thus, despite the many advantages of these existing methods, there still appears a need for methodology capable of producing variously substituted cyclopropanes in an even more highly selective fashion. Earlier we reported on the use of samarium amalgam/diiodomethane to cyclopropanate allylic alcohols in high yields, often with

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