NMR ($CDCl_3$) δ 4.1–4.4 (m, 2 H), 6.5 (dd, 1 H), 7.7 (s, 2 H). Anal. Calcd for $C_8H_5OBr_3$: C, 26.9; H, 1.4. Found: C, 26.7; H, 1.4.

**Reactions of CMA with Vinyl Ethers.** Equimolar amounts of CMA and a vinyl ether (isobutyl, phenyl, and tribromophenyl) were mixed in chloroform and kept at room temperature or at 70 °C for the latter. The occurrence of pyran **14** and **17** was proven by NMR spectroscopy. As shown in our previous paper,[16] the proton in the α-position of the ether function was responsible for a doublet of doublets peak pattern in the 5–6-ppm region. Adduct**10**: NMR δ 5.4 (dd). Adduct **11**: NMR δ 6.1 (dd). The yields of pyran and copolymer were determined by NMR spectroscopy.

**Acknowledgment.** We are deeply indebted to the National Science Foundation, Grant DMR-78-09290, to the U.S. Army Research Office, Grant DAAG-29-77-G-0231, and to Crowder College, Neosho, MO, for a leave of absence to J.W.R.

**Registry No. 1a**, 69327-00-0; **1b**, 108-31-6; **2c**, 78-79-5; **2d**, 106-99-0; **2e**, 126-99-8; **3ac**, 80698-25-5; **3ad**, 80698-26-6; **3ae**, 80698-27-7; **3bc**, 1694-82-2; **3bd**, 935-79-5; **3be**, 14180-91-7; **4c**, 74503-42-7; **4d**, 13358-22-0; **4e**, 80698-28-8; **5**, 80698-29-9; **6**, 80698-30-2; **7b**, 80698-31-3; **8**, 80698-32-4; **9**, 80698-33-5; **10**, 80698-21-1; **11**, 80698-34-6; **12**, 80698-35-7; **13**, 80698-36-8; **14**, 80698-37-9; **15**, 80698-22-2; **16**, 80698-23-3; **17**, 80698-38-0; TCNE, 670-54-2; anthracene, 120-12-7; furan, 110-00-9; cyclopentadiene, 542-92-7; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; anethole, 104-46-1; 1,1-diphenylethylene, 530-48-3; MCA 1,1-diphenylethylene copolymer, 80698-24-4; phenyl vinyl ether, 766-94-9; tribromophenyl vinyl ether, 3748-03-6; isobutyl vinyl ether, 109-53-5.

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# Absolute Rate Constants for the Reactions of *tert*-Butoxyl with Ethers: Importance of the Stereoelectronic Effect[†]

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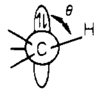
*Received July 28, 1981*

Absolute rates of hydrogen atom abstraction by *tert*-butoxyl from a variety of cyclic and acyclic ethers, orthoformates, and acetals have been measured at 27 °C by laser flash photolysis techniques. High rates of abstraction from the C–H bond adjacent to oxygen and forming small dihedral angle (ca. 30°) with the π-type orbital(s) on the oxygen(s) have been observed. For larger dihedral angles (ca. 90°) the rate of C–H abstraction is much lower. Arrhenius parameters have also been measured for a few representative cyclic ethers.

It now seems well established that stereoelectronic effects are important in heterolytic[1–5] and homolytic[6–13] chemistry. According to the principle enunciated by Deslongchamps,[1] the molecular reactivities of certain classes of compounds are determined by the relative orientation of the bond being broken or formed and the lone pair(s) on the heteroatom(s) adjacent to the reaction center.

The theoretical rationalization of such an effect is based on the concept of conjugative delocalization[14] between the electron pair(s) and the nonbonded carbon orbital ψ of the reaction center. The extent of the delocalization is a function of the dihedral angle, θ, between the C–H bond and the orbital(s) on the heteroatom(s).

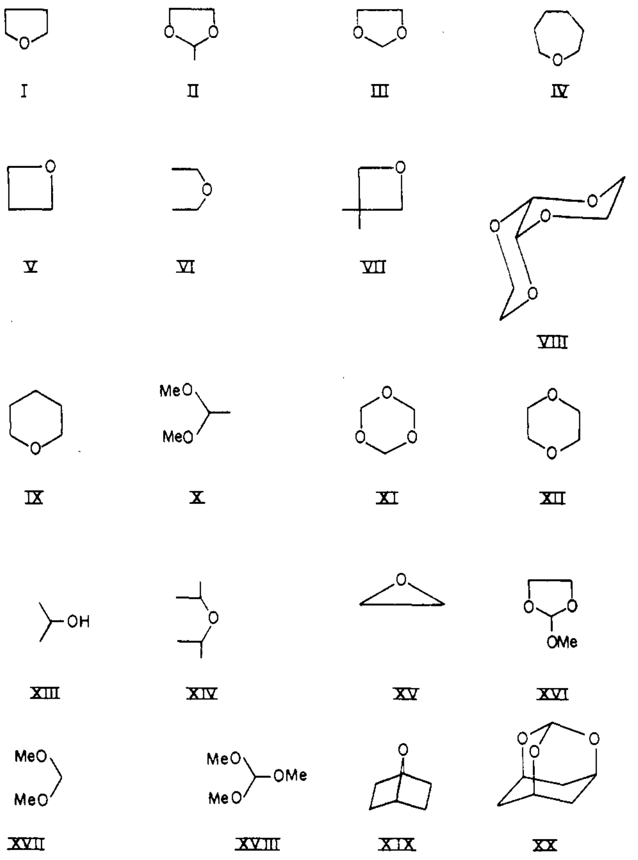


The posit of such a rationalization is an energetic and orientational nonequivalence of the heteroatom lone pairs,[15] and there is ample experimental support for this assumption.

For instance, photoelectron spectroscopy studies[16] have shown that one of the two lone pairs of electrons on oxygen is essentially a pure p type of higher energy (lower IP), with the second being approximately an s-type orbital characterized by a lower energy (higher IP).

A series of recent papers[11,13] has pointed out the importance of the stereoelectronic effects in H atom abstraction reactions from cyclic and acyclic ethers and amines. We have now extended this study to include substrates for which it is difficult or impossible to determine rate constants by an EPR technique, frequently because of difficulties in observing the EPR spectra of

Chart I



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[†] Issued as NRCC-20057.

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various corresponding alkoxyalkyl radicals, when these are expected to be multilined due to extensive hyperfine interaction of the unpaired electron with neighboring atoms.

By using nanosecond laser flash photolysis techniques, we have been able to confirm some of our earlier observations on the reactivity of ethers, orthoformates, and acetals and extend our investigation of the incidence of the stereoelectronic effect on the molecular reactivity to a wider range of substrates, including smaller size heterocycles like oxacyclobutanes and cyclic compounds characterized by a greater conformational flexibility (pseudorotation), e.g., oxacycloheptane. Chart I summarizes the structures examined.

For a few substrates, the temperature dependence of the rate constants was also studied, and the corresponding activation parameters were determined.

## Results

All measurements were carried out under oxygen-free conditions by using nanosecond laser flash photolysis techniques. The samples were excited with the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser, and the resulting transient absorptions were monitored with a detection system with nanosecond response. *tert*-Butoxyl radicals were produced by direct photodecomposition of di-*tert*-butyl peroxide. The solvent chosen for the room-temperature experiments was a 1:2 mixture of benzene and di-*tert*-butyl peroxide (v/v); the mixture is the same as that used in earlier studies, thus making the comparison of data straightforward.[17-20] For the variable-temperature studies benzene was replaced by toluene in order to allow a wider temperature range.

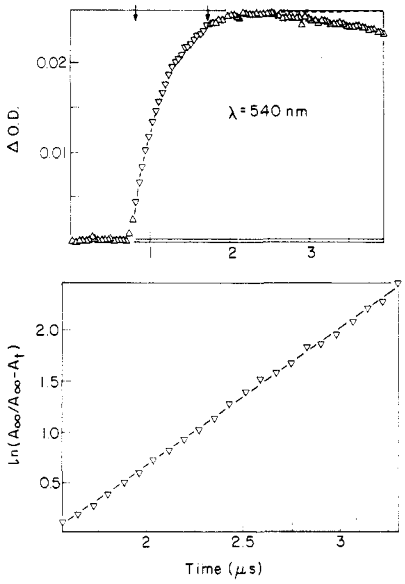

**Figure 1.** Reaction of *tert*-butoxyl with diphenylmethanol at 300 K monitored at 540 nm: *top*, OD trace; bottom, plot according to eq 5.

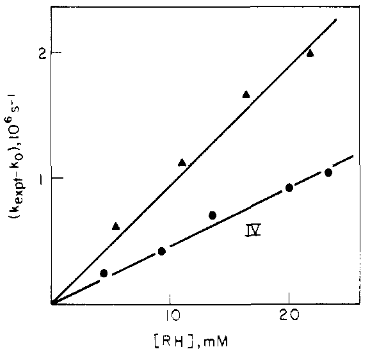

**Figure 2.** Plot according to eq 6 for II and IV at 300 K.

Alkoxy radicals can be detected directly in laser photolysis experiments of this type.[21] However, the signals produced in this manner are too weak to allow detailed kinetic studies, particularly if one takes into consideration that in order to minimize the occurrence of second-order processes, it is usually necessary to attenuate considerably the excitation dose.[18] For these reasons we have preferred to use the technique developed earlier,[17,18] which makes use of diphenylmethanol as a probe. In this method the transient signals monitored are those due to the diphenylhydroxymethyl radical, which shows a strong band at 540 nm.[22] The following sequence (eq 1–4) shows the reactions of interest in a system containing diphenylmethanol and a substrate RH.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2\ t\text{-BuO}\cdot \tag{1}$$

$$t\text{-BuO}\cdot \xrightarrow{k_d} \text{pseudo-first-order decay} \tag{2}$$

$$t\text{-BuO}\cdot + \text{Ph}_2\text{CHOH} \xrightarrow{k_p} t\text{-BuOH} + \text{Ph}_2\dot{\text{C}}\text{OH} \tag{3}$$

$$t\text{-BuO}\cdot + \text{RH} \xrightarrow{k_x} t\text{-BuOH} + \text{R}\cdot \tag{4}$$

The formation of diphenylhydroxymethyl radicals is experimentally detected as a first-order buildup following laser excitation of the sample. The first-order rate constant associated with that buildup, $k_{expt}$, can be obtained

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Table I. Reactivities of Ethers, Orthoformates, and Acetals toward *tert*-Butoxyl Radicals at 27 °C[a]

| no. | substrate | $10^6 k_x$, $M^{-1}$ $s^{-1}$ | $k_x/k_{THF}$[b] |
|---|---|---|---|
| | diphenylmethanol | 7.2 | |
| I | tetrahydrofuran | 8.25 | 1.0 |
| II | 2-methyl-1,3-dioxolane | 11.6 | 1.5 |
| III | 1,3-dioxolane | 7.7 | 0.93 |
| IV | oxacycloheptane | 4.4 | 0.54 |
| V | oxacyclobutane | 4.0 | 0.48 |
| VI | diethyl ether | 3.9 | 0.47 |
| VII | 3,3-dimethyl-1-oxacyclobutane | 3.2 | 0.39 |
| VIII | *cis*-1,4,5,8-tetraoxadecaline | 3.4 | 0.41 |
| IX | tetrahydropyran | 2.7 | 0.33 |
| X | 1,1-dimethoxyethane | 2.3 | 0.27 |
| XI | 1,3,5-trioxane | 1.95 | 0.24 |
| XII | 1,4-dioxane | 1.50 | 0.18 |
| XIII | 2-propanol | 1.80 | 0.22 |
| XIV | diisopropyl ether | 1.20 | 0.14 |
| XV | ethylene oxide | 1.1[c] | 0.13 |
| XVI | 2-methoxy-1,3-dioxolane | 1.00 | 0.12 |
| XVII | dimethoxymethane | 0.84 | 0.10 |
| XVIII | trimethoxymethane | 0.60 | 0.06 |
| XIX | 7-oxabicyclo[2.2.1]heptane | 0.35 | 0.04 |
| XX | trioxaadamantane | *d* | |

[a] Solvent is 1:2 benzene/di-*tert*-butyl peroxide. [b] Relative reactivity on a molecular basis (not per hydrogen as in earlier publications).[11] [c] ±30% due to experimental problems. [d] No reaction detected.

from a plot of ln $A_\infty/(A_\infty - A_t)$ vs. time ($t$), where $A_\infty$ and $A_t$ are the transient absorbances in the "plateau" region (see Figure 1) and at the time $t$, respectively, according to eq 5.

$$\ln A_\infty/(A_\infty - A_t) = k_{expt}t \qquad (5)$$

The parameter $k_{expt}$ is related to the rate constants of reactions 1–4 according to eq 6.

$$k_{expt} = k_d + k_p[Ph_2CHOH] + k_x[RH] \qquad (6)$$

And the values of $A_\infty$ follow the proportionality of eq 7.

$$A_\infty \propto \frac{k_p[Ph_2CHOH]}{k_d + k_x[RH] + k_p[Ph_2CHOH]} \qquad (7)$$

The addition of RH to a series of samples containing a constant concentration of diphenylmethanol leads to faster kinetics (as measured by $k_{expt}$) and to a decrease in the plateau values. The apparent enhancement of the rate of $Ph_2\dot{C}OH$ formation reflects the fact that the kinetics for the buildup is simply a measure of the lifetime of the *tert*-butoxy radicals. Figure 1 shows a representative trace (top) and the corresponding plot according to eq 5, while Figure 2 shows plots according to eq 6 (corrected for $k_0 \equiv k_d + k_p[Ph_2CHOH]$) for two of the substrates examined. The rate constants obtained from similar studies on a variety of substrates have been summarized in Table I. It should be emphasized that rate constants obtained by this technique correspond to molecular reactivity regardless of site of attack and mechanism of reaction; these usually need to be established by alternative techniques.[18] Our recent EPR study of several of the systems examined herein[11] seems to confirm that the predominant site of attack is at C–H bonds $\alpha$ to the ether bridge.

While the number of substrates for which absolute reactivities toward alkoxy radicals have been determined has been growing rapidly during the last few years,[17-20,23,24] the cases where the activation parameters are known are limited to a few hydrocarbons, ethers, and phenols.[24,25] We have chosen a few representative molecules and examined the temperature dependence of their reactions with *tert*-butoxyl radicals. While it is not strictly necessary to know the activation parameters for diphenylmethanol in order to determine those for other substrates, the corresponding values were also measured and are included in Table II. Figure 3 shows two representative Arrhenius plots.

Table II. Activation Parameters for Representative Ethers and Diphenylmethanol

| no. | substrate | log $A$,[a,b] | $E_a$,[a] kcal $mol^{-1}$ |
|---|---|---|---|
| I | tetrahydrofuran | 8.7 ± 0.8 | 2.5 ± 1.0 |
| III | 1,3-dioxolane | 9.1 ± 0.7 | 3.0 ± 0.8 |
| II | 2-methyl-1,3-dioxolane | 8.63 ± 0.26 | 2.09 ± 0.32 |
| | diphenylmethanol | 8.37 ± 0.28 | 1.99 ± 0.35 |

[a] Errors correspond to 95% confidence limits. [b] $A$ is in units of $M^{-1}$ $s^{-1}$.

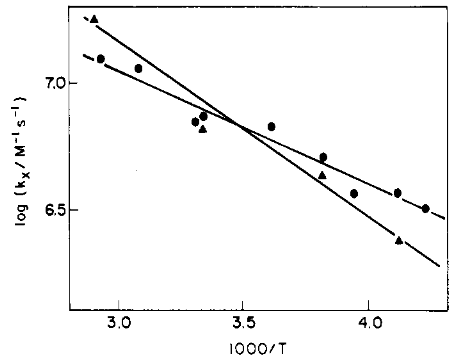

**Figure 3.** Arrhenius plots for diphenylmethanol (○) and for III (△).

## Discussion

In our previous study[11] aimed at assessing the importance of the stereoelectronic effect, we found that the "site" reactivities of the C–H bonds in cyclic and acyclic ethers nicely fit the pattern predicted on the basis of the dihedral angle/reactivity relationship. It is generally observed that relatively small dihedral angles (ca. 30°) for C–H bonds adjacent to oxygen are responsible for a pronounced stereoelectronic effect which produces high rates of H atom abstraction. On the other hand, C–H bonds having a large dihedral angle (ca. 90°) with respect to the $\pi$-type orbital(s) on the oxygen(s) undergo a much slower abstraction.

While the kinetic EPR technique allows one to measure the relative reactivity of individual C–H bonds provided that the corresponding radicals are observable, its drawbacks become evident when one tries to measure the rates of highly reactive substrates or molecules that lead to complex multiline EPR spectra. In addition, several assumptions regarding the relative rates of radical self-ter~~mination are necessary and~~ have been discussed elsewhere.[11]

The laser flash photolysis technique is not subject to the limitations of the EPR method but can only provide molecular (rather than site) reactivity; this can be transformed into absolute site reactivity if the relative importance of attack at different sites can be established. In this sense

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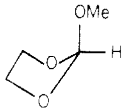
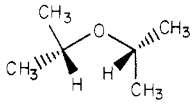
the two techniques are mutually complementary.

What emerges from our laser photolysis study can be summarized as follows. (1) A $CH_2$ in the $\alpha$-position to *one* oxygen atom is more reactive in a four- or five-membered cyclic compound than in the acyclic or six-membered cyclic counterpart. The observed enhanced reactivity of the cyclic compound is a consequence of a well-defined dihedral angle which, from Drieding molecular models, can be estimated to be ca. 30°. (2) A tertiary hydrogen atom is a cyclic acetal is more reactive than a secondary hydrogen (cf. II and III), and the same pattern is observed for the acyclic acetals (cf. XVII and X). (3) For the orthoformates (cf. XVI and XVIII) the presence of a third alkoxy group on the central carbon atom leads to a decreased reactivity of the tertiary H atom. This trend is not a consequence of an increased steric hindrance of reaction center as, for instance, 2-methyl-1,3-dioxolane (II) and 1,1-dimethoxyethane (X) are more reactive than 2-methoxy-1,3-dioxolane (XVI) and trimethoxymethane (XVIII), respectively. On the other hand it is well-known that a methyl group hinders a reaction center more effectively than a methoxy group. The observed reactivity pattern must be a reflection of the fact that stereoelectronic effects are at work (e.g., compare II and XVI). From our previous EPR work[11] we find that the reactivities of the $\beta$-$CH_2$ in the two compounds are not very different. The differences in the values of the molecular reactivities observed by flash photolysis must be due to differences in the reactivity of the C(2)–H bond. Because of the anomeric effect, the methoxy group in XVI adopts a pseudoaxial conformation, forcing the H atom into the pseudoequatorial position with a consequent increase of the $\theta$ values for the two ring oxygens.

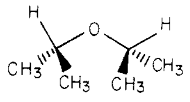


The lower reactivity of the C(2)–H in oxacyclobutane (V), while unexpected on the basis of the $\theta$ value, is not completely unreasonable. This four-membered ring is known to be, from microwave,[27] NMR,[28] IR,[29] and PES[30] studies, essentially planar ("puckering" angle of ca. 0°), with a barrier (43 cal/mol) separating the two puckered minima[31] clearly below the ground vibrational level. The vibrations of the molecules can therefore be regarded as those of a planar configuration. The dihedral angle between the C(2)–H bond and the $\pi$-type lone pair on the adjacent oxygen atom is ca. 32°[27]. It is tempting to suggest that, because of the better defined geometry and consequently a better defined value of $\theta$ in the oxetane, the reactivity of this molecule should be considered as a reference value. The C(3)–H bonds do not seem to contribute significantly to the reactivity of the oxetane as the reactivity value found for 3,3-dimethyloxacyclobutane is comparable to the one for the parent compound when allowance is made for the steric hindrance brought about by the geminal $CH_3$ groups.

The reactivity of diisopropyl ether, which from our previous study[18] seemed difficult to rationalize when compared to that of 2-propanol, is now easily understood in terms of the stereoelectronic effect. The most stable rotamer in the diisopropyl ether should exist in an all-gauche conformation, XIVa, rather than in the more sterically crowded zig-zag (all-anti) conformation, XIVb.

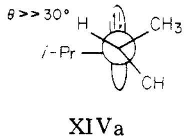


XIVa



XIVb

In the rotamer XIVa, the dihedral angle $\theta$ between the C–H bond and the $\pi$-type lone pair is ≫30° so that the nonbonded repulsive interactions are minimized.

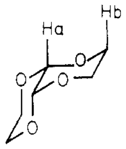


XIVa

The large value of the dihedral angle accounts for the lower reactivity of the C–H bond in diisopropyl ether. No preferential conformation effects are expected for 2-propanol for which the "average" value of the dihedral angle should be smaller than the one expected for XIVa.

Although accurate rate constant measurements for the H atom abstraction in trioxaadamantane (XX) are difficult because of the poor solubility of this substrate in the benzene/di-*tert*-butyl peroxide mixture, we estimate that $k \ll 10^6$ $M^{-1}$ $s^{-1}$. This confirms our previous observation on the difficulty of measuring the reactivity of this substrate by an EPR kinetic technique which, we believe, was due to the fact that a radical characterized by a complex multilined spectrum would be formed by abstraction of the apical or of any other type of hydrogen atom present in the molecule.

For *cis*-1,4,5,8-tetraoxadecaline (VIII) the observed molecular reactivity value is about half of the one measured for tetrahydrofuran (I) while by kinetic EPR we find a relative value of 0.26. The difference, we believe, is due to some reactivity at $H_b$ which is anticipated to be as reactive as $H_a$ on the basis of the dihedral angle value but would lead to a complex EPR spectrum.



VIII

A value of 2.3 kcal/mol was estimated[11] for the activation energy for H abstraction from tetrahydrofuran by taking a preexponential factor for H atom abstraction from ethers to be $5 \times 10^8$ $M^{-1}$ $s^{-1}$. The measured activation parameters of a few representative ethers (Table II) are in excellent agreement with the above estimated value.

Finally, we comment on the observed reactivity trend for cyclic systems of different sizes. We find that the absolute rate constants decrease along the ring-size series $5 > 7 > 4 > 6 > 3$.[12]

We attribute the greater reactivity of C–H bonds in five-membered rings to a combination of higher conformational mobility and to a rate acceleration induced by a relief of ring strain. The seven-membered rings are also characterized by high conformational mobility and are

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Table III. Hyperfine Coupling Constants of Some Typical Radicals and Normalized Rates of Hydrogen Abstraction

| radical | $a(\alpha\text{-H})$, G | temp, K | ref | $10^4k_x/(\text{H})$,[b] $M^{-1}\ s^{-1}$ |
|---|---|---|---|---|
| α-tetrahydropyranyl (IX – H·) | −15.8 | 300 | 32 | 65 |
| cyclohexyl | −21.3 | 193 | 33 | 13.3[a] |
| α-tetrahydrofuranyl (I – H·) | −12.4 | 300 | 34 | 206 |
| cyclopentyl | −21.5 | 300 | 35 | 8.8 |
| oxiranyl (IV – H·) | +24.5 | 243 | 36 | 27.5 |
| cyclopropyl | −6.66 | 179 | 37 | $\leqslant 0.17$ |

[a] J. A. Howard, private communication. [b] At 27 °C.

expected to be more reactive than the more rigid four- and six-membered-ring systems.

Ethylene oxide (XVI) is a rather interesting case, and its relatively low rate constant tends to mask the true magnitude of the stereoelectronic effect. We know for example that cyclopentane ($k_x = 8.8 \times 10^5$) is far more reactive than cyclopropane, which is frequently regarded as a good "inert" solvent for alkoxy radical reactions. The value of $k_x$ for cyclopropane is no doubt lower than $\sim 10^4$ $M^{-1}\ s^{-1}$, a limit that reflects hybridization differences between five- and three-membered rings. When we compare the hydrocarbons and heterocycles, we find a reactivity enhancement of a factor of ca. 5 for the six-membered ring, of ca. 24 for the five-membered ring, and of over 160 for the three-membered ring (Table III).

This behavior seems to suggest that stabilizing interactions, i.e., conjugative delocalization and back-hyperconjugation[38] in the oxacycloalk-2-yl radical, which are expected to be more effective because of conformational requirements in the three- and five-membered rings, are responsible for the larger reactivity enhancement in the case of ethylene oxide and tetrahydrofuran. An inspection of the relative values of the hfcc's for the α-H of the oxacycloalk-2-yl radical (Table III) shows that the radical formed upon H atom abstraction from ethylene oxide has a much larger (and positive) hfcc than the tetrahydropyran-2-yl radical.

It is well established[14,38] that this indicates a more pyramidal geometry at the radical center and therefore a more effective conjugative delocalization and back-hyperconjugation. For the tetrahydropyran-2-yl radical formed by abstraction of the axial H atom, only a weak conjugative delocalization is expected; furthermore, this stabilizing interaction and back-hyperconjugation cannot occur in the radical formed by abstraction of the equatorial H atom. Therefore, for the six-membered ring, no substantial reactivity difference is expected between the cycloalkane and the corresponding oxacycloalkane.

## Experimental Section

**Materials.** Di-*tert*-butyl peroxide (MC&B) was treated on an alumina column in order to eliminate traces of *tert*-butyl hydroperoxide. Diphenylmethanol (Aldrich) was sublimed twice, and special care was taken to eliminate any traces of benzophenone. The ethers, orthoformates, and acetals used in this study were either commercial materials or were prepared according to literature procedures.[11] They were purified by preparative gas chromatography (Varian 920) on a 12 ft × $^3/_8$ in., 12% Carbowax 20M on 60/80 Chromosorb WHP column at 120 °C or on a 12 ft × $^3/_8$ in., 20% OV-101 on 45/60 HP Chromosorb W column at 95–110 °C. *cis*-1,4,5,8-Tetraoxadecalin was crystallized twice from diethyl ether. 1,3,5-Trioxane was sublimed and then crystallized from a mixture of ethanol/ether (1:1). The liquid materials were stored in the dark over $K_2CO_3$.

**Laser Flash Photolysis.** The samples, usually 1 mL, were contained in Suprasil cells made from 3 × 7 mm$^2$ rectangular tubing (Vitro Dynamics) and were deaerated by using oxygen-free nitrogen. A Molectron UV-24 nitrogen laser was used for excitation. The signals were received in a Tektronix R-7912 transient digitizer; our facility has been fully interfaced with a PDP 11/03L computer which controls the experiment, averages and processes data, and provides suitable storage and hard-copy facilities. Further details have been published elsewhere.[26]

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**Registry No.** I, 109-99-9; I–H·, 19426-60-9; II, 497-26-7; III, 646-06-0; IV, 592-90-5; V, 503-30-0; VI, 60-29-7; VII, 6921-35-3; VIII, 13405-83-9; IX, 142-68-7; IX-H·, 25088-30-6; X, 534-15-6; XI, 110-88-3; XII, 123-91-1; XIII, 67-63-0; XIV, 108-20-3; XV, 75-21-8; XI-H·, 31586-84-2; XVI, 19693-75-5; XVII, 109-87-5; XVIII, 149-73-5; XIX, 279-49-2; XX, 281-32-3; di-*tert*-butyl peroxide, 110-05-4; diphenylmethanol, 91-01-0; cyclopentyl radical, 3889-74-5; cyclopropyl radical, 2417-82-5.

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[38] Brunton, G.; Ingold, K. U.; Roberts, B. P.; Beckwith, A. L. J.; Krusic, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 3177.

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# Contamination of 4-Substituted 1,2,4-Triazoline-3,5-diones with Urazolyl Radicals

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4-Substituted 1,2,4-triazoline-3,5-diones as normally prepared are contaminated with free radicals, which cannot be removed by sublimation or recrystallization. Solutions of these compounds contain urazolyl radicals in equilibrium with a dimer. On standing at room temperature for a few days, the urazolyl radical rearranges to a new radical, which is also in equilibrium with a dimer. The ESR spectra of these radicals are discussed and structures proposed. The presence of these free-radical initiators may have important consequences on the mechanisms of some of the thermal and photochemical reactions of triazolinediones.

In 1968, we had an occasion to prepare 4-phenyl-1,2,4-triazoline-3,5-dione (**1a**) with the expectation of using it in some cycloaddition reactions. In the course of those investigations we made some observations that led us to