Structural Effects on the β-Scission Reaction of Alkoxyl Radicals. Direct Measurement of the Absolute Rate Constants for Ring Opening of Benzocycloalken-1-oxyl Radicals

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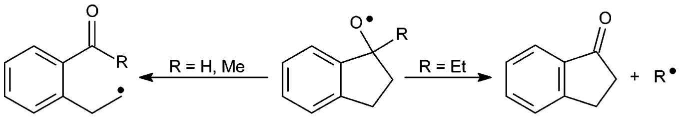
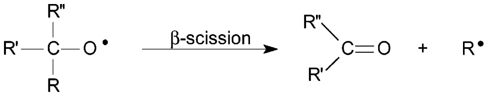


The absolute rate constants for β-scission of a series of benzocycloalken-1-oxyl radicals and of the 2-(4-methylphenyl)-2-butoxyl radical have been measured directly by laser flash photolysis. The benzocycloalken-1-oxyl radicals undergo ring opening with rates which parallel the ring strain of the corresponding cycloalkanes. In the 1-X-indan-1-oxyl radical series, ring opening is observed when X = H, Me, whereas exclusive C−X bond cleavage occurs when X = Et. The factors governing the fragmentation regioselectivity are discussed.

C−C β-scission leading to a carbonyl compound and an alkyl radical is one of the most important reactions of alkoxyl radicals (Scheme 1), and accordingly, considerable attention has been devoted to the study of this reaction.[2−7]

One of the main conclusions of these studies has been that with tertiary alkoxyl radicals cleavage generally leads to the most stable possible alkyl radical, even though it has also been shown that in the reactions of 1-alkylcycloalkoxyl radicals other factors such as the release of ring strain associated to ring opening may play an important role.[6,8−10] On the other hand, kinetic studies leading to the determination of absolute rate constants for β-scission of alkoxyl radicals in solution are still limited,[11−23] most of these studies concerning the reactivity of the *tert*-butoxyl[15−17] and cumyloxyl[18−23] radicals. In particular, when dealing with the ring-opening reactions of cycloalkoxyl radicals the only data available have been obtained for the cyclopentoxyl and cyclohexoxyl radicals by means of competitive kinetics as $k = 4.7 \times 10^8$ and 1.1×10^7 s^{-1}, respectively.[24] Results which are in line with those obtained in relative reactivity studies,[10] and

SCHEME 1



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SCHEME 2

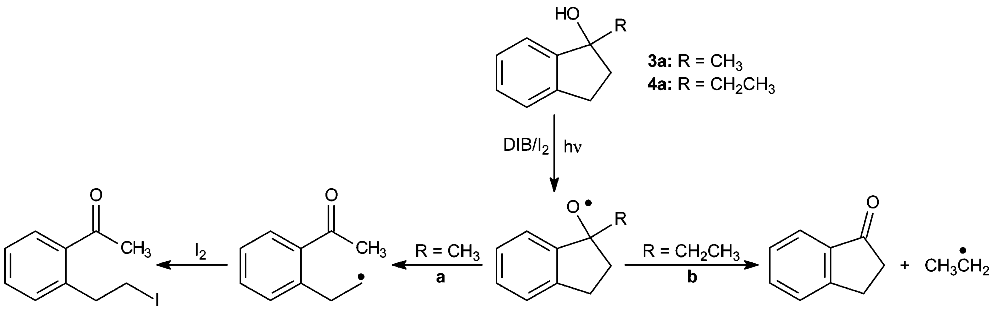
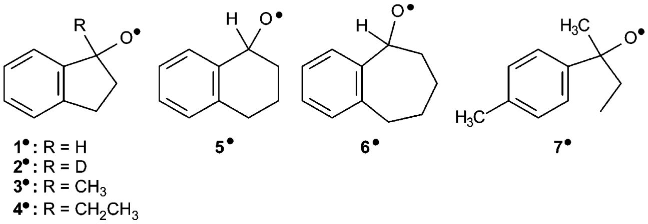


CHART 1



which have been rationalized in terms of the greater ring strain associated to a five-membered ring as compared to a six membered one.

The recent discovery that arylcarbinyloxyl radicals display an absorption band in the visible region of the spectrum[25] makes possible the direct measurement of alkoxyl radical reactivity by laser flash photolysis.[18−20,26] Along this line, to obtain kinetic information on the ring opening reaction of cycloalkoxyl radicals, we have carried out a time-resolved kinetic study on the reactivity of a series of benzocycloalken-1-oxyl radicals (**1**$^{\bullet}$−**6**$^{\bullet}$) whose structures are shown in Chart 1. As a matter of comparison, the study has been extended to the 2-(4-methylphenyl)-2-butoxyl radical (**7**$^{\bullet}$),[27] a tertiary alkoxyl radical which is structurally related to **3**$^{\bullet}$ and **4**$^{\bullet}$, lacking however the rigidity imposed by the presence of the five-membered ring.

With radicals **3**$^{\bullet}$, **4**$^{\bullet}$, and **7**$^{\bullet}$ it is possible, at least in principle, to obtain two different C−C bond fragmentations. Previous studies have shown that the 2-phenyl-2-butoxyl radical undergoes exclusive C-ethyl bond cleavage,[28] and an analogous behavior can be reasonably expected for **7**$^{\bullet}$. No information is instead available for **3**$^{\bullet}$ and **4**$^{\bullet}$. Thus, to obtain information on the fragmentation regioselectivity of **3**$^{\bullet}$ and **4**$^{\bullet}$ we have also carried out product studies generating the radicals photochemically by visible light irradiation of CH_2Cl_2 solutions containing the parent 1-alkylindanols, (diacetoxy)iodobenzene (DIB), and I_2.[8,29]

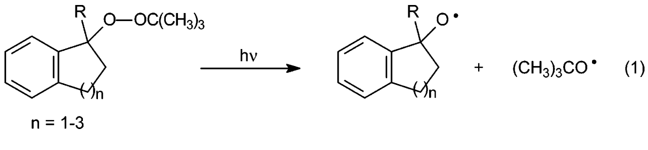
Results and Discussion

Product Studies. Argon-saturated CH_2Cl_2 solutions containing 1-methylindanol (**3a**) or 1-ethylindanol (**4a**) (10 mM), DIB (11 mM), and I_2 (10 mM) were irradiated with visible light ($\lambda_{max} \approx 480$ nm) at $T = 20$ °C. The irradiation time was chosen in such a way as to avoid complete substrate conversion. After workup of the reaction mixture, the reaction products were identified by GC−MS and ^{1}H NMR and quantitatively determined, together with the unreacted substrate by GC and ^{1}H NMR, using bibenzyl as internal standard.

The reaction of **3a** led to the formation of 2-(2-iodoethyl)acetophenone as the exclusive reaction product. 1-Indanone was instead the exclusive product observed with **4a**. Formation of these products can be explained in terms of the β-scission reaction of the intermediate 1-alkylindan-1-oxyl radicals **3**$^{\bullet}$ and **4**$^{\bullet}$ as described in Scheme 2.

With the 1-methylindan-1-oxyl radical (**3**$^{\bullet}$) exclusive ring-opening occurs followed by rapid reaction of the ring-opened carbon centered radical with iodine[32,33] to give 2-(2-iodoethyl)acetophenone (path **a**). The 1-ethylindan-1-oxyl radical (**4**$^{\bullet}$) undergoes instead exclusive C-ethyl bond cleavage to give 1-indanone (path **b**).

Time-Resolved Studies. Benzocycloalken-1-oxyl radicals (**1**$^{\bullet}$−**6**$^{\bullet}$) were generated by ns 248 or 266 nm laser flash photolysis (LFP) of the parent *tert*-butyl-benzocycloalken-1-yl peroxides (**1p**−**6p**: between 2.0 and 5.6 $\times$ 10^{-3} M) in argon or oxygen saturated MeCN solution (eq 1).



All benzocycloalken-1-oxyl radicals displayed an absorption band in the UV region of the spectrum between

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(26) Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527−3531.

(27) The *tert*-butyl-2-(4-methylphenyl)-2-butyl peroxide (**7p**) was chosen because, as compared to the ring-unsubstituted one, the presence of a methyl group ensured a significantly higher absorption at the laser excitation wavelength (266 nm). As discussed previously for cumyloxyl radicals (see ref 18), the reactivity should not be affected by the presence of the ring-substituent.

(28) Hawkins, E. G. E. *J. Chem. Soc.* **1949**, 2076−2077.

(29) It is well established that under these conditions the DIB/I_2 reagent converts alcohols into intermediate hypoiodites which are then photolyzed to give alkoxyl radicals, precursors of the observed reaction products (see, for example, refs 30 and 31).

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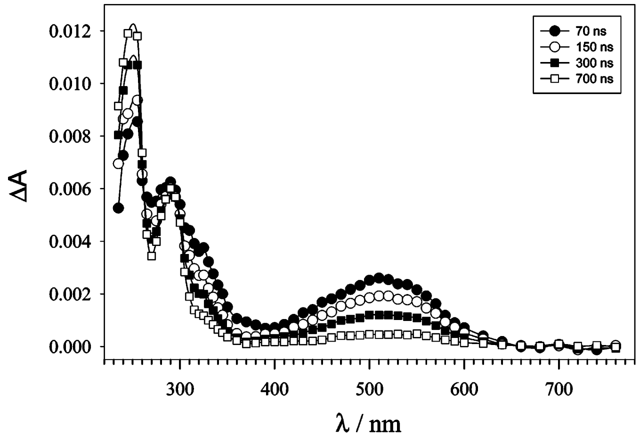


FIGURE 1. Time-resolved absorption spectra observed after 248 nm LFP of an oxygen-saturated MeCN solution containing 4×10^{-3} M *tert*-butyl-1-tetralyn peroxide (**5p**) at 70 (filled circles), 150 (empty circles), 300 (filled squares), and 700 ns (empty squares) after the 20 ns, 20 mJ laser flash.

320 and 350 nm, and a broad absorption band in the visible region between 500 and 530 nm depending on radical structure.[25] Both bands were found to be unaffected by oxygen and were observed to decay following first-order kinetics. A more intense band centered around 280 nm was also observed which however was found to undergo a much slower decay and which is assigned to the *tert*-butoxyl radical on the basis of the comparison with literature data.[16,18,34] Decay of the benzocycloalken-1-oxyl radical bands led in all cases to a corresponding strong increase in absorption in the UV region of the spectrum which, again, was found to be unaffected by oxygen and which is assigned to the ring-conjugated carbonyl product formed after β-scission (see below).

As an example, Figure 1 shows the time-resolved absorption spectra obtained after 248 nm LFP of an oxygen saturated MeCN solution containing *tert*-butyl-1-tetralyn peroxide (**5p**). No significant spectral difference was observed when the experiment was carried out in argon-saturated solution. The spectrum recorded 70 ns after the laser flash (filled circles) shows two absorption bands centered at 320 and 520 nm which, in agreement with previous studies, are assigned to the tetralyn-1-oxyl radical ($\mathbf{5}^{\bullet}$).[25a] This species undergoes a first-order decay accompanied by a corresponding buildup of optical density at 240 nm assigned to the carbonyl product $2\text{-HCOC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2^{\bullet}$ formed by C−C β-scission of $\mathbf{5}^{\bullet}$ (Scheme 3).[35]

A relatively more stable absorption band centered at 280 nm is also observed which, as described above, is assigned to the *tert*-butoxyl radical.[16,18]

An analogous behavior was observed after 248 nm LFP of a MeCN solution containing *tert*-butyl-1-indanyl peroxide (**1p**), as shown in Figure 2. The indan-1-oxyl radical ($\mathbf{1}^{\bullet}$) visible absorption band was red-shifted by 10 nm,[25a] and relatively less intense as compared to $\mathbf{5}^{\bullet}$, and underwent a first-order decay accompanied by a corresponding buildup of optical density at 245 nm assigned to $2\text{-HCOC}_6\text{H}_4\text{CH}_2\text{CH}_2^{\bullet}$.

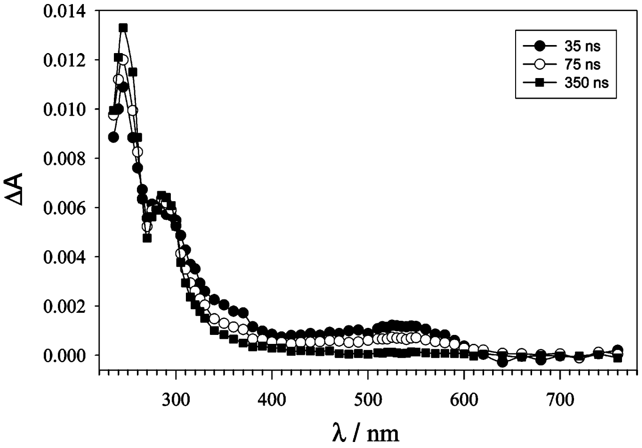
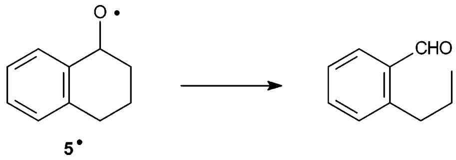
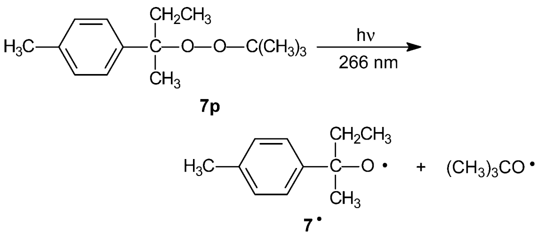


FIGURE 2. Time-resolved absorption spectra observed after 248 nm LFP of an oxygen-saturated MeCN solution containing 4×10^{-3} M *tert*-butyl-1-indanyl peroxide (**1p**) at 35 (filled circles), 75 (empty circles), and 350 ns (filled squares) after the 20 ns, 20 mJ laser flash.

SCHEME 3



The 2-(4-methylphenyl)-2-butoxyl radical ($\mathbf{7}^{\bullet}$) was instead generated by 266 nm ps LFP of *tert*-butyl-2-(4-methylphenyl)-2-butyl peroxide (**7p**) in MeCN (eq 2).



(2)

A visible absorption band centered at 510 nm appeared immediately after the 20 ps laser pulse (Figure 3a), which can be reasonably assigned to the 2-(4-methylphenyl)-2-butoxyl radical ($\mathbf{7}^{\bullet}$).

This radical was observed to undergo a first-order decay on the nanosecond time-scale (Figure 3b) which, on the basis of product studies,[28] is assigned to C-ethyl bond cleavage (Scheme 4).

The experimental rate constants for decay of radicals $\mathbf{1}^{\bullet}$−$\mathbf{7}^{\bullet}$ were measured spectrophotometrically by monitoring the decrease in absorption at the visible absorption maximum of the radicals and/or the increase in absorption in the UV region around 240 nm and are collected

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[34] An extinction coefficient $\epsilon_{280} = 560\ \text{M}^{-1}\ \text{cm}^{-1}$ has been determined for the *tert*-butoxyl radical in MeCN solution (see ref 16). Since identical amounts of the *tert*-butoxyl and benzocycloalken-1-oxyl radicals $\mathbf{1}^{\bullet}$−$\mathbf{6}^{\bullet}$ are produced after LFP of peroxides **1p**−**6p**, the extinction coefficients of the UV and visible absorption bands of radicals $\mathbf{1}^{\bullet}$−$\mathbf{6}^{\bullet}$ are smaller than this value.

[35] The 240 nm band is assigned to the radical $2\text{-HOCC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2^{\bullet}$ which is expected to react rapidly with oxygen. However, since this band is associated to the ring-conjugated carbonyl chromophore, it is not expected to be influenced by the reaction with oxygen.

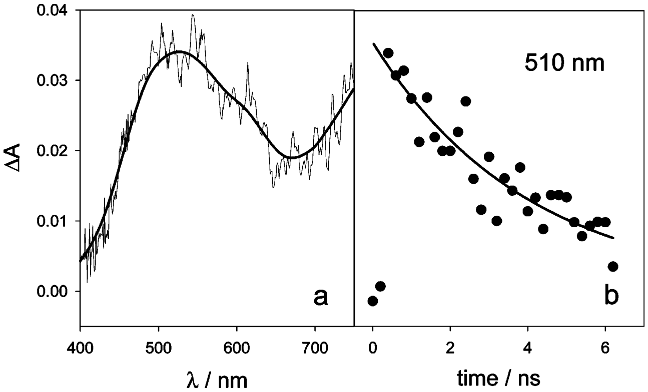
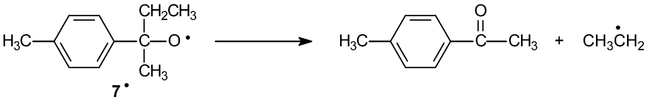


FIGURE 3. (a) Transient absorption spectrum observed after 266 nm LFP of an air-saturated MeCN solution containing 1.5 × 10^{-2} M *tert*-butyl-2-(4-methylphenyl)-2-butyl peroxide (**7p**) at 100 ps after the 20 ps laser pulse. (b) Decay kinetics monitored at 510 nm.

SCHEME 4



in Table 1, together with the corresponding data for the 4-methylcumyloxyl radical.

The spectral data displayed in Table 1 show that the position of the visible absorption band of benzocycloalken-1-oxyl radicals is not influenced to a significant extent by the ring size and by the presence of an alkyl substituent in position 1, in agreement with previous studies.[25a] For what concerns instead the 2-(4-methylphenyl)-2-butoxyl radical (**7•**), the visible absorption band is centered at 510 nm in line with the value observed for the 4-methylcumyloxyl radical,[18,25] again indicating that the position of the visible absorption band is not influenced by small modifications in side-chain structure.

Table 1 also shows the values of the rate constants for β-scission of the radicals **1•**−**7•**. In the indan-1-oxyl series, with the exclusion of **4•** (see below), the value of k_β is not influenced by the nature of the group in position 1 (H, D, Me), the three radicals (**1•**−**3•**) undergoing ring opening with the same rate constant: $k_\beta = 1.3 \times 10^7$ s^{-1}. This result is apparently in contrast with those obtained recently by Newcomb and Horner for a series of alkoxyl radicals,[11] showing that the fragmentation rate constant increased as a function of the carbonyl compound produced in the fragmentation reaction in the order CH_2O < MeCHO < Me_2CO. Clearly, the observation of identical rate constants for **1•** and **3•** suggests that with these radicals the release of ring strain associated to the five member ring opening is significantly more important than the stability of the carbonyl product formed.

The comparison between the rate constants for **1•** and **2•** shows that, as expected, replacement of H by D does not influence the transition state for β-scission.

The 1-ethylindan-1-oxyl radical (**4•**) was instead found to undergo β-scission with a significantly higher rate constant than those measured for radicals **1•**−**3•**, in a reaction which, on the basis of product studies, is assigned to C-ethyl bond cleavage. An observation which indicates that in contrast with **3•**, where no C-methyl cleavage was observed, with **4•** the fragmentation regioselectivity is essentially governed by the greater stability of the ethyl radical as compared to the methyl one and by the entropy gain associated to the C-ethyl cleavage, whereas the release of ring strain associated to ring opening plays a minor role.

TABLE 1. Visible Absorption Band Maximum Wavelengths for Radicals (1•−7•) and Kinetic Data for Their Decay by β-Scission (k_β) in MeCN

radical		λ_{max} (vis)/nm[a]	k_β/s^{-1} [b]	T/°C
indan-1-oxyl	**1•**	530	1.3 × 10^7	22
1-deuterioindan-1-oxyl	**2•**	530	1.3 × 10^7	22
1-methylindan-1-oxyl	**3•**	520	1.3 × 10^7	22
1-ethylindan-1-oxyl	**4•**	520	≥8 × 10^{7c}	0
			1.2 × 10^7	−15
tetralyn-1-oxyl	**5•**	520	8.2 × 10^{5d}	22
benzosuberyl-1-oxyl	**6•**	500	1.5 × 10^{6d}	22
2-(4-methylphenyl)-2-butoxyl	**7•**	510	2.5 × 10^8	22
			≥8 × 10^{7c}	0
			1.1 × 10^7	−15
4-methylcumyloxyl		510	7.1 × 10^{5e}	22

[a] Visible absorption band maximum of the radical. [b] Determined by following the decay of the radical at the visible absorption maximum and/or the buildup of the carbonyl product formed after C−C β-scission at 240 nm. [c] Under these conditions, the radical was too reactive to be studied by ns LFP, and on the basis of the buildup at 240 nm, only a lower limit could be determined. [d] A dependence of the decay rate on laser energy was observed, and the rate constants were extrapolated from the intercepts of the rate constant vs laser energy plots (see the Supporting Information). [e] Taken from ref 18.

Unfortunately, the weak visible absorption band of **4•** [34] did not allow LFP studies on the picosecond time-domain, and due to the high reactivity of this radical, k_β was determined by nanosecond LFP only at $T = -15$ °C, whereas at $T = 0$ °C only a lower limit ($k_\beta \geq 8 \times 10^7$ s^{-1}) could be determined.[36]

Quite interestingly, the observation that **4•** undergoes exclusive C-ethyl bond cleavage whereas ring opening was the only fragmentation pathway observed for the 1-ethylcyclopentoxyl radical[8] suggests that, due to the rigidity imposed by the presence of the fused phenyl ring, the release of ring strain associated to ring opening is relatively less important in the former radical as compared to the latter one. Another factor which may also account for this behavior is represented by the fact that, as compared to the 1-ethylcyclopentoxyl radical, in **4•** C-ethyl bond cleavage can be assisted by the overlap between this bond and the aromatic π system.[25a]

Comparison between the rate constants for ring opening of the benzocycloalken-1-oxyl radicals[37] points toward the importance of ring strain in governing the reactivity of these radicals. The observed reactivity order, k_β (**1•**) > k_β (**6•**) > k_β (**5•**), to which correspond the following relative reactivities, 15.8:1.8:1, parallels the ring strain of the corresponding cycloalkanes.[38] Interestingly, an analogous

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(36) As a matter of comparison, also the reactivity of radical **7•** was studied at $T = -15$ and 0 °C (see Table 1).

(37) Unfortunately, attempts to synthesize the *tert*-butyl benzocyclobutenyl peroxide from the parent benzocyclobuten-1-ol failed.

(38) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.

reactivity order was observed for the nucleophilic ring-opening reactions of cyclic dimethylammonium ions.[39]

It is also very interesting to compare the k_β value measured for the 2-(4-methylphenyl)-2-butoxyl radical ($\mathbf{7}^\bullet$), $k_\beta = 2.5 \times 10^8$ s^{-1}, with that measured previously for the 4-methylcumyloxyl radical: $k_\beta = 7.1 \times 10^5$ s^{-1}.[18] The comparison shows that in tertiary arylcarbinyloxyl radicals ethyl radical ejection occurs 350 times faster than that of a methyl radical, a result which is in line with those obtained in previous studies, based however on relative reactivities.[4,5b,13]

Compounds $\mathbf{7}^\bullet$, $\mathbf{3}^\bullet$, and $\mathbf{4}^\bullet$ can be considered structurally related tertiary arylcarbinyloxyl radicals (Chart 1), the former one lacking the rigidity imposed by the presence of the five-membered ring. Thus, comparison between the rate constants for β-scission measured for these radicals may provide useful information on the effect of radical structure on reactivity. As mentioned above, $\mathbf{3}^\bullet$ undergoes exclusive ring-opening whereas C-ethyl cleavage is the exclusive reactive pathway for both $\mathbf{4}^\bullet$ and $\mathbf{7}^\bullet$. The rate constants collected in Table 1 show that $\mathbf{7}^\bullet$ undergoes β-scission ~20 times faster than $\mathbf{3}^\bullet$, a result which suggests that the entropy gain associated to the C-ethyl cleavage in the former radical is relatively more important than the release of ring strain associated to the five-membered ring opening in $\mathbf{3}^\bullet$. For what concerns instead the comparison between $\mathbf{4}^\bullet$ and $\mathbf{7}^\bullet$, even though it was not possible to measure the rate constant for β-scission of $\mathbf{4}^\bullet$ at room temperature, the data collected in Table 1 point toward similar reactivities for these two radicals. This observation suggests that in the β-scission reactions of arylcarbinyloxyl radicals which lead to the formation of the same alkyl radical the stability of the carbonyl product formed in the fragmentation reaction plays a minor role. This result is in line with those obtained recently for the β-scission reactions of a series of ring-substituted cumyloxyl radicals.[18]

In conclusion, the absolute rate constants for ring-opening of a series of benzocycloalken-1-oxyl radicals have been measured directly by laser flash photolysis. The radicals undergo ring opening with rates which parallel the ring strain of the corresponding cycloalkanes. In the 1-X-indan-1-oxyl radical series ring-opening is observed when X = H, Me, whereas exclusive C−X bond cleavage occurs when X = Et, a behavior which indicates that the fragmentation regioselectivity is essentially governed by the interplay between the stability of the radical formed by C−X bond cleavage, entropic effects, and the release of ring strain associated to ring opening.

Experimental Section

Materials. MeCN of the highest available purity was used as received. Commercial samples of indan-1-ol (**1a**) and tetral-1-ol (**5a**) were used without further purification. Details on the synthesis of the arylcarbinols (**2a**−**4a**, **6a**, **7a**) and of the *tert*-butyl arylcarbinyl peroxides (**1p**−**7p**) are given in the Supporting Information.

Product Studies. The reactions were carried out under an argon atmosphere. Dichloromethane was purified prior to use by column chromatography over basic alumina. Irradiations were performed with visible light (10 × 15 W lamps with emission between 400 and 550 nm, $\lambda_{\max} \approx 480$ nm). The reactor was a cylindrical flask equipped with a water cooling jacket thermostated at 20 °C. Irradiation times were chosen in such a way as to avoid complete substrate consumption. In a typical experiment, a solution of the alcohol **3a** or **4a** (10 mM) in CH_2Cl_2 (5 mL) containing (diacetoxy)iodobenzene (11 mM) and iodine (10 mM) was irradiated for times varying between 5 and 10 min under Ar bubbling. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with a 10% aqueous thiosulfate solution (2 × 30 mL) and water (2 × 30 mL) and dried over anhydrous sodium sulfate. Reaction products were identified by GC−MS and ^{1}H NMR and quantitatively determined, together with the unreacted substrate by GC and ^{1}H NMR, using bibenzyl as internal standard. Good mass balances (≥85%) were obtained in all experiments.

The reaction of **3a** led to the formation of 2-(2-iodoethyl)-acetophenone as the exclusive reaction product. After workup, 2-(2-iodoethyl)acetophenone was isolated from the reaction mixture by preparative TLC (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC−MS, ^{1}H NMR, and ^{13}C NMR. GC−MS *m/z* (relative abundance): M$^+$ 146, 131, 127, 116, 115 (100), 103, 91, 89, 77, 63, 51, 50. ^{1}H NMR ($CDCl_3$): δ 7.74−7.26 (m, 4H), 3.41 (s, 4H), 2.61 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 201.3, 140.7, 137.1, 132.0, 130.1, 127.1, 126.4, 38.8, 29.5, 6.2.

The reaction of **4a** led to the formation of 1-indanone (identified by comparison with an authentic sample) as the exclusive reaction product. No effort was made to detect the formation of ethyl iodide.

Time-Resolved LFP Studies. Benzocycloalken-1-oxyl radicals $\mathbf{1}^\bullet$−$\mathbf{6}^\bullet$ were generated at room temperature by direct laser flash photolysis (LFP) of the corresponding *tert*-butyl peroxides (**1p**−**6p**), using a 248 nm excimer laser (KrF*, Lambda Physik EMG103MSC) providing 20 ns pulses with energies between 5 and 60 mJ/pulse (output power of the laser). Optical detection was employed with a pulsed xenon lamp as analyzing light. Wavelengths were selected using a monochromator. The time-dependent optical changes were recorded with Tektronix 7612 and 7912 transient recorders, interfaced with a DEC LSI 11/73$^+$ computer, which also controlled the other functions of the instrument and preanalyzed the data.[40] Argon- or oxygen-saturated solutions of the peroxides (between 2.0 and 5.6 × 10^{-3} M: $A_{248} \approx 0.3$−0.6) in MeCN were flowed through a 2 mm (in the direction of the laser beam) × 4 mm (in the direction of the analyzing light, 90° geometry) Suprasil quartz cell. All experiments were carried out at 22 ± 2 °C. Rate constants were obtained by averaging 6−12 values, each consisting of an average of 10−50 laser shots, and were reproducible to within 10%.

Some experiments were also carried out employing a Nd:YAG laser (266 nm), providing 8 ns pulses with energies between 5 and 20 mJ/pulse (output power of the laser), irradiating argon-saturated MeCN solutions of peroxides **4p** or **7p** (1.5 and 3.8 × 10^{-3} M, respectively: $A_{266} \approx 1$), contained in a 3 mL Suprasil quartz cell (10 mm × 10 mm) under magnetic stirring. The experiments were carried out at 0 and −15 °C. As a matter of comparison, peroxide **1p** was also studied under these conditions at $T = 22$ °C, and a value of k_β for fragmentation of $\mathbf{1}^\bullet$ identical to that measured employing 248 nm LFP ($k_\beta = 1.3 \times 10^7$ s^{-1}) was obtained.

The 2-(4-methylphenyl)-2-butoxyl radical ($\mathbf{7}^\bullet$) was generated by direct LFP of *tert*-butyl-2-(4-methylphenyl)-2-butyl peroxide (**7p**), using 266 nm light (fourth harmonic of a Nd:YAG laser, Continuum PY61C-10) providing 20 ps pulses with energies between 2 and 3 mJ/pulse. A solution of the peroxide (1.5 × 10^{-2} M: $A_{266} \approx 1$) in MeCN was flowed through a 2 mm (in the direction of the pump) × 4 mm (in the direction of the

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probe, 90° geometry) quartz cell. All experiments were carried out at 22 ± 2 °C. The picosecond spectrometer and the methods of data handling have been described in detail previously.[41]

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Supporting Information Available: Details on the synthesis and characterization of the precursor arylcarbinols and *tert*-butyl arylcarbinyl peroxides. Plots of the decay rate constants against laser energy for radicals **5**$^{\bullet}$ and **6**$^{\bullet}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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