Supporting Information

Structural Effects on the β-Scission Reaction of Tertiary Arylcarbinyloxyl Radicals. The Role of α-Cyclopropyl and α-Cyclobutyl Groups

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1) Synthesis of arylalkanols 1a, 4a-6a

1-Cyclopropyl-1-phenylethanol (**1a**) was prepared by reaction of methylmagnesium chloride with cyclopropylphenyl ketone in anhydrous tetrahydrofuran, purified by column chromatography (neutral alumina, eluent hexane/ethyl acetate 5:1) and identified by ^{1}H NMR.[S1]

^{1}H NMR ($CDCl_3$): δ 7.55-7.51 (m, 2H), δ 7.37-7.31 (m, 2H), δ 7.28-7.22 (m, 1H), δ 1.61 (s, 1H), δ 1.49 (s, 3H), δ 1.31-1.21 (m, 1H), δ 0.57-0.34 (m, 4H).

1-Cyclobutyl-1-phenylethanol (**4a**) and *1-cyclobutyl-1-phenylpropanol* (**5a**) were prepared by reaction of cyclobutyl phenyl ketone with methylmagnesium and ethylmagnesium chloride, respectively, in anhydrous tetrahydrofuran, purified by column chromatography (neutral alumina, eluent hexane/ethyl acetate 5:1) and identified by ^{1}H NMR and GC-MS.

4a: ^{1}H NMR ($CDCl_3$): δ 7.32-7.22 (m, 5H), δ 2.81-2.69 (m, 1H), δ 2.12-1.57 (m, 7H), δ 1.43 (s, 3H). GC-MS m/z (relative abundance): 158, 143, 129, 121 (100), 115, 105, 91, 77, 55, 51.

5a: ^{1}H NMR ($CDCl_3$): δ 7.35-7.21 (m, 5H), δ 2.86-2.80 (m, 1H), δ 2.09-1.51 (m, 9H), δ 0.69 (t, 3H). GC-MS m/z (relative abundance): 172, 161, 143, 135, 129, 115, 105, 91, 77, 57 (100).

α,α-Dicyclobutylphenylmethanol (**6a**) was prepared by reaction of cyclobutyl phenyl ketone with cyclobutylmagnesium chloride, which in turn was prepared by reaction of cyclobutyl chloride with magnesium in anhydrous tetrahydrofuran; purified by column chromatography (neutral alumina, eluent hexane/ethyl acetate 5:1) and identified by ^{1}H NMR and GC-MS.

^{1}H NMR ($CDCl_3$): δ 7.30-7.18 (m, 5H), δ 2.83-2.77 (m, 2H), δ 2.08-1.48 (m, 13H).

GC-MS m/z (relative abundance): 198, 170, 161 (100), 155, 142, 128, 117, 115, 105, 91, 77, 55.

2) Synthesis of peroxides 1p, 2p and 4p

tert-Butyl 1-cyclopropyl-1-phenylethyl peroxide (**1p**), *tert-butyl α,α-dicyclopropylbenzenemethyl peroxide* (**2p**), and *tert-butyl 1-cyclobutyl-1-phenylethyl peroxide* (**4p**), were prepared by reaction of the corresponding phenylalkanols **1a**, **2a** and **4a** with *tert*-butyl hydroperoxide in the presence of *p*-toluenesulfonic acid, according to a slight modification of a previously described procedure.[S2] A 5.0-6.0 M solution of *tert*-butyl hydroperoxide in decane was added to a solution of the phenylalkanol (*tert*-butyl hydroperoxide/alcohol ≈ 1.2) in CH_2Cl_2 (purified prior to use by column chromatography over basic alumina) containing *p*-toluenesulfonic acid (phenylalkanol/acid ≈ 10). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. *tert*-Butyl 1-phenylalkyl peroxides were purified by column chromatography (Florisil, eluent pentane) and identified by ^{1}H NMR.

tert-Butyl 1-cyclopropyl-1-phenylethyl peroxide (**1p**): ^{1}H NMR ($CDCl_3$): δ 7.50-7.47 (m, 2H), δ 7.34-7.22 (m, 3H), δ 1.46 (s, 3H), δ 1.31-1.26 (m, 1H), δ 1.25 (s, 9H), δ 0.52-0.30 (m, 4H).

tert-Butyl α,α-dicyclopropylbenzenemethyl peroxide (**2p**): ^{1}H NMR (CDCl$_3$): δ 7.60-7.55 (m, 2H), δ 7.34-7.21 (m, 3H), δ 1.26 (s, 9H), δ 1.20-1.09 (m, 2H), δ 0.64-0.30 (m, 8H).

tert-Butyl 1-cyclobutyl-1-phenylethyl peroxide (**4p**): ^{1}H NMR (CDCl$_3$): δ 7.26-7.20 (m, 5H), δ 2.64-2.51 (m, 1H), δ 2.07-1.96 (m, 6H), δ 1.57 (s, 3H), δ 1.26 (s, 9H).

3) Laser flash photolysis (LFP) studies

Figure S1 displays the time-resolved spectra observed after LFP of an argon saturated MeCN solution containing peroxide **2p**, showing after 160 ns (filled circles) a very broad absorption band extending from approximately 550 nm down to the UV region, characterized by absorption maxima around 490, 420 and 360 nm, which is assigned to the radical **2**$^\bullet$. This species undergoes a first-order decay accompanied by a corresponding buildup of optical density at 250 nm assigned to cyclopropyl phenyl ketone. Also visible is a relatively stable absorption band centered at 280 nm which, on the basis of the comparison with literature data,[S3,S4] is assigned to the *tert*-butoxyl radical. The slight increase in absorption observed at 280 nm is attributed to the formation of cyclopropyl phenyl ketone, which is also characterized by a weak absorption band centered at 276 nm.

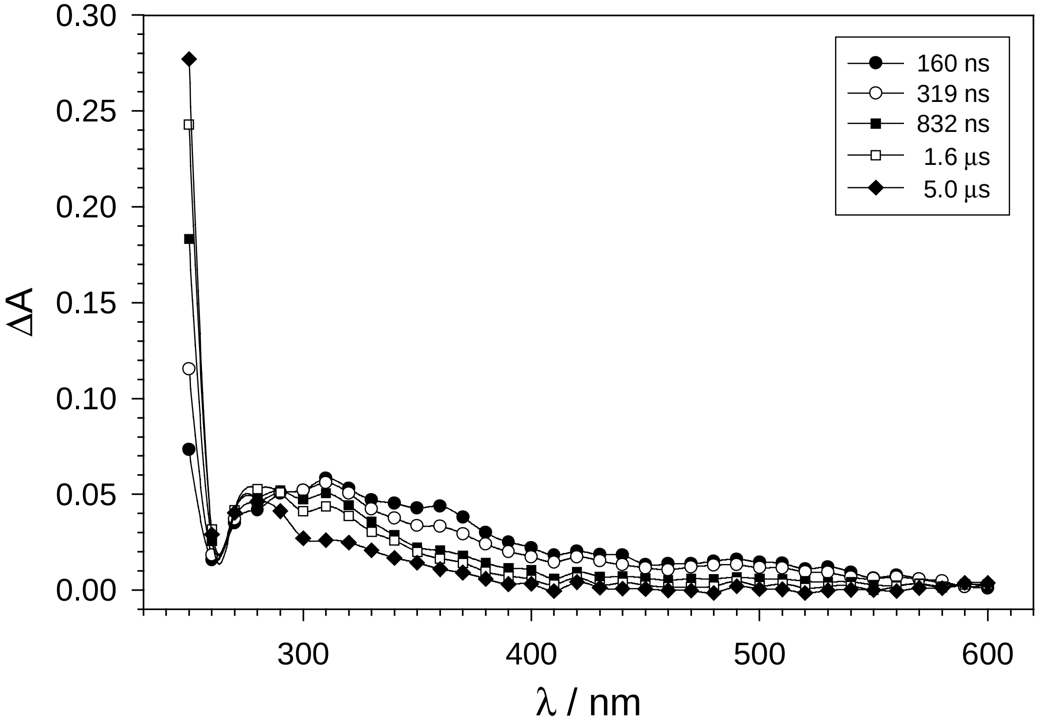

Figure S1. Time-resolved absorption spectra observed after 266 nm LFP of **2p** (10.0 mM) in an argon-saturated MeCN solution at 160 ns (filled circles), 319 ns (empty circles), 832 ns (filled squares), 1.6 μs (empty squares), and 5.0 μs (filled diamonds) after the 8 ns, 10 mJ laser pulse.

4) References

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