Reactivity toward oxygen of isobenzofuranyl radicals: Effect of nitro group substitution

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SUPPORTING INFORMATION

Experimental Section

Reagents and Products. TEMPO, di-tert-butyl peroxide, di-cumyl peroxide and compounds **1** and **3** were commercially available. Ciba Irganox® HP-136 was a gift from CIBA Specialty Chemicals. Synthesis of di-α-cumyl hyponitrite and compounds **2**, **4**, **5**, and **7** has been previously described.[1-4]

3-(3-Trifluoromethyl-phenyl)-3*H*-isobenzofuran-1-one (6). Syntheis of **6** was carried out using 1-bromo-3-trifluoromethyl-benzene as starting material and following the procedure published for **7**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.4 (s, 2 H), 7.3 (d, *J* = 8 Hz, 1 H), 7.4 – 7.7 (m, 6 H), 7.9 (d, *J* = 8 Hz, 1 H); MS *m/z* 278 (M^+, 50), 259 (15), 209 (21), 133 (35), 105 (100), 77 (33). M. p. 97-98 ^{O}C. Anal. Calcd for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26; F, 20.49. Found: C, 64.71; H, 3.34; F, 20.61.

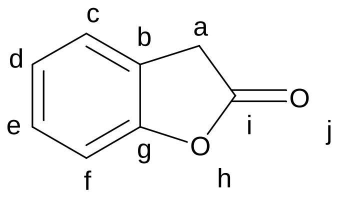
Laser Flash Photolysis. The radicals were generated from the corresponding compounds by laser excitation of *tert*-butyl-peroxide in benzene using 355 nm pulses from a Continuum Nd-YAG Surelite. Excitation at 355 nm was used for direct photolysis of haloalkane **2**. Transient signals were captured with a digital oscilloscope which was interfaced to a computer which also controlled the experiment. The system was operated with software written in the LabVIEW 5.1 environment from National Instruments. All experiments were carried out using static cells constructed from 7 x 7 mm Suprasil quartz tubing. Samples were purged with a slow stream of either nitrogen or oxygen, as required.

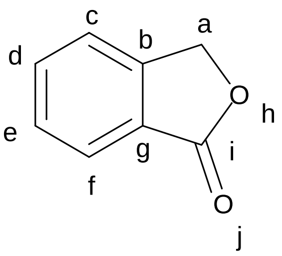
Thermolysis of di-α-cumyl hyponitrite.[1] This method was used to determine the reactivity of cumyloxyl radicals toward phthalides **3-7**. Thermolysis of di-cumyl hyponitrite was carried out in deaerated benzene at 30 ^{0}C for 12 hours in the presence of various substrate concentrations (0-70 mM).

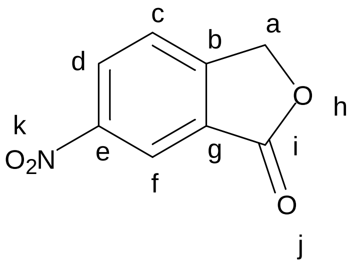
The relative yields of 2-phenyl-2-propanol (A) and acetophenone (K) were determined by gas cromatography. The plot of A/K vs. [RH] yields k_a/ k_β from the slope.

k_a is the rate constant for the hydrogen atom abstraction and k_β is the rate constant for the β scission. The values of k_a for compounds **3**-**7** were obtained using k_a determined for Ciba Irganox® HP-136 using laser flash photolysis techniques[5] and di-cumyl peroxide as source of cumyloxyl radicals

Spin distribution for benzyl radicals.







		Radical from	
	2-coumaranone	**3*H*-isobenzofuran-1-one**	**6-nitro-phthalide**
a	+45.3	+52.4	+47.3
b	-4.9	-5.1	-2.8
c	+14.9	+12.4	+11.4
d	-4.4	-3.4	-0.6
e	+22.1	+15.1	+13.2
f	-6.5	-3.5	-4.9
g	+15.8	+13.5	+12.2
h	-1.1	+2.7	+3.9
i	+1.7	+4.7	+3.4
j	+20.9	+15.3	+13.9
k			+5.6

References

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