Evidence for Divalent Iodine (9-I-2) Radical Intermediates in the Thermolysis of (*tert*-Butylperoxy)iodanes. An Unusually Efficient Deiodination of *o*-Iodocumyl Alcohols by Cyclohexyl Radicals[1]

Darko Dolenc and Božo Plesničar*

Contribution from the Department of Chemistry, University of Ljubljana, P.O. Box 537, 1000 Ljubljana, Slovenia

Received October 18, 1996. Revised Manuscript Received January 21, 1997[⊗]

Abstract: 1-(*tert*-Butylperoxy)-3,3-dimethyl-1*H*-1,2-benziodoxoles (**2a** and **2b**) and 1-(*tert*-butylperoxy)-3,3-bis-(trifluoromethyl)-5-methyl-1*H*-1,2-benziodoxole (**2c**) were prepared from chloroiodanes **1a−c** and *tert*-butyl hydroperoxide in the presence of potassium *tert*-butoxide in tetrahydrofuran. Products, kinetic data for the decomposition of **2** in cyclohexane, benzene, toluene, and acetonitrile (E_a = 31.0 ± 1.0 kcal/mol, log A = 17.0 ± 0.5; 35−70 °C), and the increased rate of decomposition of **2c** in benzene-d_6 in the presence of a magnetic field (7 T) indicate that homolytic cleavage of the I−O bond in **2** with the formation of iodanyl (9-I-2) and *tert*-butylperoxyl radicals is the primary decomposition step. The nearly quantitative formation of iodocyclohexane during the decomposition of **2c** in cyclohexane is due to the unexpected reaction of cyclohexyl radicals with 2-(2-iodo-5-methylphenyl)-1,1,1,3,3,3-hexafluoro-2-propanol, a primary decomposition product of **2c**. The results of a separate study of the deiodination of *o*-iodocumyl alcohols (**3**) by cyclohexyl radicals are consistent with an S_H2 type mechanism.

Introduction

Although diaryl- and dialkyliodonium ions are well-established,[2] relatively little is known about divalent iodine (9-I-2) radicals.[3] Such intermediates have been proposed in a number of synthetically and theoretically[4] important reactions, but no direct ESR evidence for their existence has as yet been reported.

Strong support for a divalent iodine radical was reported by Tanner et al. in a study of the kinetics for the transfer of the iodine atom from an aryl iodide to an aryl radical.[5] Most recently, Scaiano et al. reported evidence for the intermediacy of a cyclic hypervalent iodine radical in the laser flash and laser-drop photolysis of 1,5-diiodo-1,5-diphenylpentane.[6a,6]

Ochiai et al. have recently prepared and characterized the first stable (alkylperoxy)iodane, i.e., 1-(*tert*-butylperoxy)-1,2-

benziodoxol-3(1*H*)-one, by Lewis acid-catalyzed (BF₃−Et₂O) exchange of the hydroxy group of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one with a *tert*-butylperoxy group.[7−9] They also provided evidence for the involvement of iodanyl radicals in its decomposition.[7b]

As a part of our continuing interest in divalent iodine radicals and in systems capable of providing such intermediates, we report a convenient synthesis of other members of the family of relatively stable (alkylperoxy)iodanes. The decomposition of these peroxides was studied. The results of a study of an unusually effective deiodination of *o*-iodocumyl alcohols by cyclohexyl radicals are also reported.

Results and Discussion

(*tert*-Butylperoxy)iodanes. Treatment of 1-chloro-3,3-dimethyl-1*H*-1,2-benziodoxoles (**1a** and **1b**) or 1-chloro-3,3-bis-(trifluoromethyl)-5-methyl-1*H*-1,2-benziodoxole (**1c**)[4d] with *tert*-butyl hydroperoxide in the presence of potassium *tert*-butoxide

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

(1) Dolenc, D.; Plesničar, B. Presented in part at the 7th International Symposium on Organic Free Radicals; Bardolino (Lake Garda), Italy, June 1996. Book of Abstracts, p 71.

(2) (a) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 274. Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996,** *96,* 1123. (b) Koser, G. F. In *The Chemistry of Functional Groups, Suppl. D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 18. (c) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990,** 431. (d) Varvoglis, A. *The Chemistry of Polycoordinated Iodine*; VCH: Weinheim, 1992.

(3) For a nomenclature, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980,** *102,* 7753. Martin, J. C. *Science* **1983,** *221,* 509.

(4) For thermally or photoinitiated chlorinations by (dichloro)iodobenzenes, see: Russell, G. A. *J. Am. Chem. Soc.* **1958,** *80,* 4987. (b) Banks, D. F.; Huyser, E. S.; Kleinburg, J. *J. Org. Chem.* **1964,** *29,* 3692 (c) Chlorinations by [chloro(*tert*-butoxy)iodo]benzene: Tanner, D. D.; Gidley, G. C. *J. Am. Chem. Soc.* **1968,** *90,* 808. (d) Chlorinations by the Martin's chloroiodanes: Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979,** *101,* 3060. *J. Org. Chem.* **1979,** *44,* 1779. (e) For the Breslow's template-directed chlorination of steroids, see: Breslow, R.; Corcoran, R.; Dale, J. A. Liu, S.; Kalicky, P. *J. Am. Chem. Soc.* **1974,** *96,* 1973. White, P.; Breslow, R. *J. Am. Chem. Soc.* **1990,** *112,* 6842, and references therein. (f) For anchimeric acceleration of *ortho*-iodo-substituted peroxides homolysis, see, for example: Martin, J. C. *ACS Symp. Ser.* **1978,** *69,* 71, and references cited therein.

(5) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982,** *104,* 3917, and references cited therein.

(6) (a) Banks, J. T.; Garcia, H.; Miranda, M. A.; Perez-Prieto, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1995,** *117,* 5049. (b) For a previous attempt to detect such an intermediate, see: Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1990,** *55,* 1061.

(7) (a) Ochiai, M.; Ito, T.; Masaki, Y.; Shiro, M. J. *J. Am. Chem. Soc.* **1992,** *114,* 6269. (b) Ochiai, M.; Ito, T.; Takahashi, H.; Nakanishi, A.; Toyonari, M.; Sueda, T.; Goto, S.; Shiro, M. *J. Am. Chem. Soc.* **1996,** *118,* 7716. (c) See also: Ochiai, M.; Ito, T.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1993,** 218.

(8) Moss et al. have prepared 1-(*tert*-butylperoxy)-1,2-benziodoxol-3(1*H*)-one by a ligand exchange of a labile (phosphoryloxy)iodane (prepared in situ by the reaction of 1-chloro-1,2-benziodoxol-3(1*H*)-one with silver diphenyl phosphate in DMSO) with *tert*-butyl hydroperoxide. Moss, R. A.; Zhang, H. *J. Am. Chem. Soc.* **1994,** *116,* 4471.

(9) [Bis(*tert*-butylperoxy)iodo]benzene was proposed as an intermediate in the low-temperature reaction of iodosobenzene with *tert*-butyl hydroperoxide, and its decomposition to iodobenzene and *tert*-butylperoxyl radicals has been reported. When the reaction was run in diethyl ether, good yields of *tert*-butylperoxy acetal were isolated. Milas, N. A.; Plesničar, B. *J. Am. Chem. Soc.* **1968,** *90,* 4450. See, also: Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1987,** *109,* 6201. (b) [Bis(benzoylperoxy)iodo]benzenes were isolated as amorphous, labile (rather hazardous) materials: Plesničar, B.; Russell, G. A. *Angew. Chem., Int. Ed. Engl.* **1970,** *9,* 797. Plesničar, B. *J. Org. Chem.* **1975,** *40,* 3267.

Scheme 1

a: $R_1 = CH_3$; $R_2 = H$
b: $R_1 = CH_3$; $R_2 = OCH_3$
c: $R_1 = CF_3$; $R_2 = CH_3$
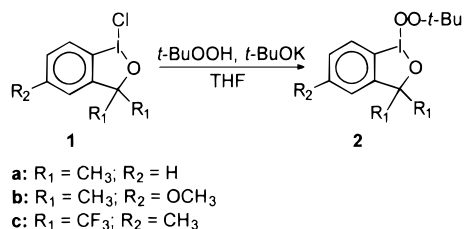
Table 1. Kinetic and Activation Parameters for the Decomposition of (*tert*-Butylperoxy)iodanes in Various Solvents[a]

(alkylperoxy)-iodane	solvent	$10^5 k$[55 °C], s^{-1}	E_a, kcal mol^{-1}	log A
2a	c-C_6D_{12}	20.7	31.4 ± 1.0	17.3 ± 0.1
2a	c-C_6D_{12}[b]	18.3	31.9 ± 1.0[b]	17.5 ± 0.1
2a	CD_3CN	107	30.2 ± 1.0	17.2 ± 0.1
2a	C_6D_6	44.7	31.7 ± 1.0	17.8 ± 0.1
2b	C_6D_6	48.4	30.8 ± 1.7	17.3 ± 0.2
2c	C_6D_6	1.42[c]	31.4 ± 1.0	15.2 ± 0.1
2c[d]	C_6D_6	1.27[c]	30.1 ± 2.0	14.3 ± 0.1

[a] Kinetic measurements were carried out in sealed NMR tubes in thermostated NMR probe (Bruker AVANCE 300 DPX, B = 7 T) unless stated otherwise. The disappearance of H7 absorption in the starting compound was in all cases measured by ^{1}H NMR. [b] One equiv of 2,6-di-*tert*-butyl-4-methylphenol was added. [c] At 70 °C. [d] Water-bath thermostat.

in tetrahydrofuran at 0 °C gave 1-*tert*-butylperoxy-1*H*-1,2-benziodoxoles (**2a−c**) in yields ranging from 50 to 60% (after crystallization). (Scheme 1). All (alkylperoxy)iodanes were fully characterized by elemental and spectral analysis. The pure crystalline solids have an indefinite shelf life when kept in the dark.

The decomposition of the (alkylperoxy)iodanes in four different solvents (cyclohexane, toluene, benzene, acetonitrile) typically in the temperature range from 35 to 70 °C was studied, by following the decay of the H7 (^{1}H NMR) absorptions of **2** as a function of time. The disappearance of the (alkylperoxy)-iodanes obeyed first-order kinetics over several half-lives in all solvents investigated. Kinetic and activation parameters for the decomposition of **2** are collected in Table 1 (Figure 1).

Solvent effects on the decomposition are relatively small; i.e., comparable rate constants (within a factor of 4−5) were obtained for the decomposition of the (alkylperoxy)iodanes in all solvents investigated. A study of the decomposition of **2a** in the presence of 2,6-di-*tert*-butyl-4-methylphenol showed a relatively small reduction in rate and nearly the same activation parameters.

Although the effect of substituents on the decomposition has not been studied systematically, it is interesting to note that electron-donating *p*-OCH$_3$ group somewhat accelerates decomposition of **2a**.

The decomposition products of peroxyiodanes are collected in Table 2. The observed products and activation parameters are indicative of homolytic cleavage of the I−O bond to form iodanyl (9-I-2) and *tert*-butylperoxyl radicals in the primary decomposition step (Scheme 2). The somewhat faster decomposition of **2c** (by a factor 1.18 ± 0.05, from the Arrhenius plot) in the cavity of the NMR instrument (7 T; singlet−triplet rephasing) compared to the decomposition run in a thermostated bath indicates that the iodanyl radical is stable enough to undergo geminate recombination with the *tert*-butylperoxyl radical in the solvent cage to regenerate the original precursor.[10]

Two surprising observations regarding the decomposition products of the (alkylperoxy)iodanes in cyclohexane deserve comment. In the decomposition of the *gem*-dimethyl derivative **2a**, large amounts of *tert*-butyl cyclohexyl peroxide were found
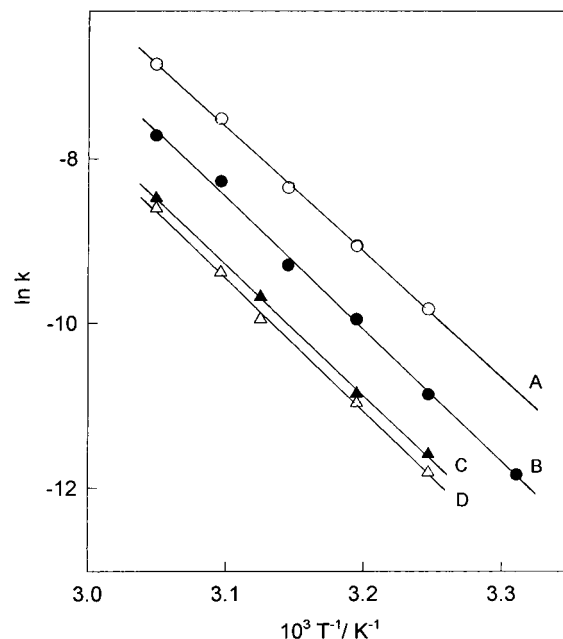
Figure 1. Arrhenius plots for the decomposition of **2a** in various solvents: A, CD_3CN; B, C_6D_6; C, Cyclohexane-d_{12}; and D, cyclohexane-d_{12} (with added 2,6-di-*tert*-butyl-2-methylphenol).

Table 2. Products of the Thermal Decomposition of **2a** and **2c** in Various Solvents[a,b]

products	2a		2c	
	cyclohexane (TEMPO)[c]	toluene	cyclohexane (TEMPO)	toluene
3a,c	90 (86)	76	3 (100)	88
4a,c	3 (4)	19	0 (0)	0
5a,c	3 (0)	0	94 (0)	0
	4 (0)	0	94 (0)	0
SOO-*t*-Bu	40 (5)	72	40 (0)	73
t-BuOOH	14 (41)	3	1 (30)	0

[a] Reactions were run in ampoules (0.05 mmol of iodane, 1 mL of solvent, Ar atmosphere) in a boiling hexane (**2a**) or cyclohexane bath (**2c**). [b] Yields of products in mol %, based on the initial amount of iodane. [c] Yields in the presence of 2 equiv of TEMPO. **3, 4, 5a:** $R_1 = CH_3$, $R_2 = H$; **3, 4, 5c:** $R_1 = CF_3$, $R_2 = CH_3$. Besides the products quoted in the table, considerable amounts of *tert*-butyl alcohol and acetone were produced as well as 20−40% of alcohol and ketone, derived from solvent (in toluene and cyclohexane). The decomposition of **2a** in benzene gave mainly ketone **4a** (56%) and alcohol **3a** (26%).

among the products (40%). Although this peroxide might result from S$_H$2 attack of the cyclohexyl radical on the oxygen atom next to iodine in **2a**, we believe that it is formed predominantly by coupling of the *tert*-butylperoxyl and the cyclohexyl radicals. In the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), an efficient radical scavenger, besides the iodo alcohol **3a**, *tert*-butyl hydroperoxide, was the main decomposition product (41%). Even larger amounts of dialkyl peroxide, i.e., benzyl *tert*-butyl peroxide, were found when toluene was the solvent.

On the other hand, the decomposition of the trifluoromethyl substituted (alkylperoxy)iodane **2c** in cyclohexane gave only
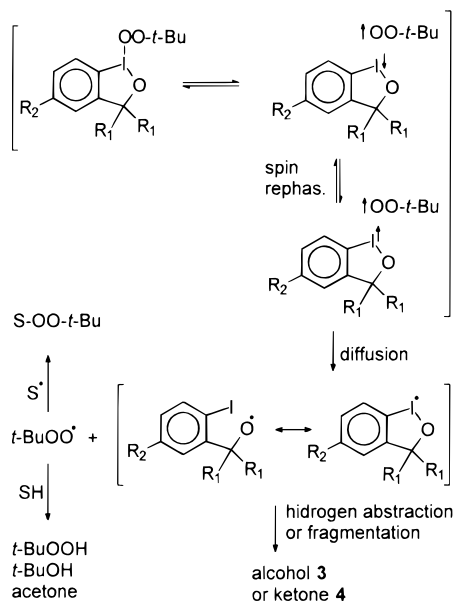
Scheme 2

Figure 2. A Hammett plot for the deiodination of substituted 2-iodophenyl-2-propanols by cyclohexyl radicals.

Table 3. Reactions of Substituted Bromo- and Iodobenzenes (X−Ar−I) with Di-*tert*-butylperoxyoxalate (DBPO) in Cyclohexane[a,b]

[a] Iodobenzene (0.1 mmol) and 0.1 mmol of DBPO in 4 mL of cyclohexane (boiling cyclohexane, 2 h, argon atmosphere). [b] Composition of the reaction mixture in mol % per mol of the starting halobenzene. [c] Bromocyclohexane.

A Hammett plot (σ) (Figure 2) gave a fair correlation with $\rho = 1.10$ ($r = 0.97$). (2) Experiments with the OD deuterated derivative of **3a** gave unlabeled iodocyclohexane and cumyl alcohol. At the same time, the reaction of unlabeled iodoalcohol with labeled cyclohexyl radicals in cyclohexane-d_{12} resulted in incorporation of deuterium into the *ipso* position of the product. (3) The absence of the cyclohexyl substituted benzylic alcohols among the reaction products and the inability of benzyl radicals (in toluene) to perform the same reaction seem to rule out the $S_{RN}1$ mechanism.[11] (4) The trifluoromethyl substituted iodo alcohol **3c** is more reactive than the *gem*-dimethyl derivative **3a** by a factor of 46 ± 3. (5) Phenyl and *n*-heptyl radicals (57 and 25% conversions, respectively, in benzene) and *tert*-butyl radicals (25%, in isobutane) were found to be less efficient than cyclohexyl radicals (in cyclohexane) in these reactions. However, the reaction conditions in these cases were not completely comparable, so that the differences in reactivity were difficult to evaluate.

Based on the above evidence, we propose an S_H2 type mechanism (Scheme 3) involving electron transfer from the cyclohexyl radical to the substituted iodobenzene, via a transition state resembling an iodobenzene radical anion-cyclohexyl cation pair, to give an aryl radical and iodocyclohexane in an essentially concerted process (pathway A). The possibility of the involvement of a discrete ion pair intermediate cannot be excluded. An alternative mechanism (pathway B) involving a divalent iodine (9-I-2) radical species (Ar−I−R), already proposed as intermediates in thermoneutral deiodinations of aryl iodides by phenyl radicals,[5] and subsequent decomposition to an aryl radical and iodocyclohexane also cannot be ruled out. However, on the basis of the somewhat greater sensitivity of reactions with cyclohexyl radicals to electronic effects, compared to that with phenyl radicals ($\rho = 0.474$, $r = 0.820$),[5] this mechanistic option appears to be less likely.

The question arises as to why *o*-iodocumyl alcohols are so much more reactive toward deiodination than other electronegatively ortho-substituted iodobenzenes studied. We believe that the enhanced reactivity is due to intramolecular hydrogen

small amounts of the iodo alcohol **3c** and nearly quantitative yields of the deiodinated cumyl alcohol **5c** and iodocyclohexane.

Deiodination of *o*-Iodocumyl Alcohols by Cyclohexyl Radicals. Since we suspected that cyclohexyl radicals initiated the abstraction of iodine from the iodo alcohol, this reaction was studied separately. When iodo alcohols **3a** and **3c** were allowed to react with cyclohexyl radicals, generated by the decomposition of di-*tert*-butyl peroxyoxalate (DBPO) in cyclohexane under argon, quantitative yields of iodocyclohexane and the corresponding benzylic alcohols were formed (Table 3). Considerably lower yields of iodocyclohexane were obtained with other electronegatively 2-substituted iodobenzenes.

Since the direct abstraction of the iodine atom by the cyclohexyl radical seemed unlikely (endothermic by 11 ± 1 kcal/mol), further experiments to elucidate the mechanism of this reaction were performed. The results of these studies can be summarized as follows: (1) The relative reactivities, determined in competition experiments of meta- and para-substituted **3a,** showed that electron-withdrawing groups accelerate deiodination while electron-releasing groups retard it.
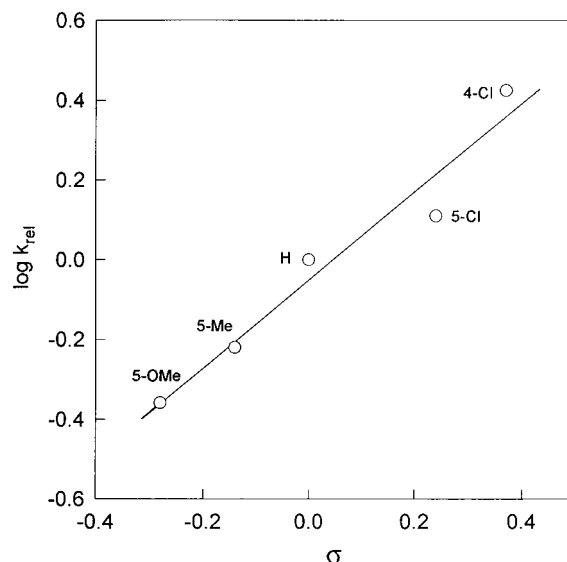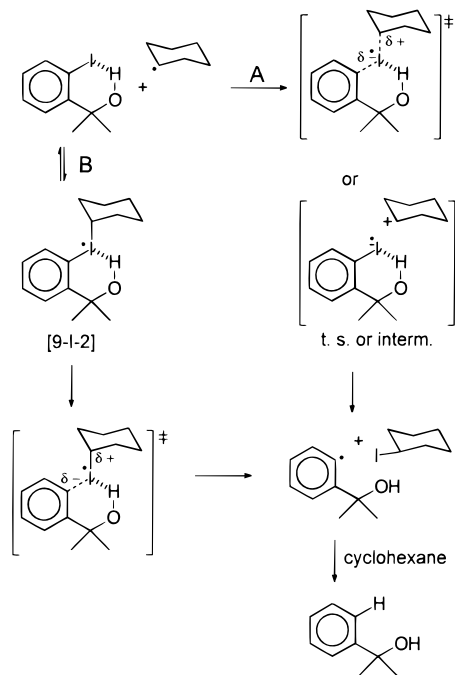
(10) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369. Buchachenko, A. L.; Khudyakov, I. V. *Acc. Chem. Res.* **1991**, *24*, 177.

(11) (a) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663. (b) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5662. (c) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413; **1992**, *25*, 2. (d) Russell, G. A. *Adv. Phys. Org. Chem.* **1987**, *23*, 271.

Divalent Iodine (9-I-2) Radical Intermediates

J. Am. Chem. Soc., Vol. 119, No. 11, 1997 2631

Scheme 3

bonding.[12] It perhaps renders these systems more susceptible to acceptance of an incoming electron into an antibonding σ^* MO of the C–I bond[13] and/or stabilizes the proposed iodine centered radical intermediate, i.e., ArI$^{\bullet-}$ (or Ar–I–R), since considerably lower yields of deiodinated products were obtained when other electronegatively 2-substituted iodobenzenes were employed. A further observation that the deiodination reactions proceed much less efficiently in cyclohexane with added "basic" hydrogen bond donors (B) (B = *tert*-butyl methyl ether ($\beta \cong$ 0.47), pyridine (0.642), *N,N*-dimethylacetamide (0.756);[14] cyclohexane:B = 4:1, v/v), capable of interrupting intramolecular hydrogen bonding by forming *o*-iodocumyl alcohol-B adducts, seems to support this presumption. With increasing hydrogen bond donor ability (β) of the added B, the efficiency of deiodination was decreasing. The fact that the *gem*-bis(trifluoromethyl) derivative **3c** is more reactive (more "acidic")[15] than the dimethyl analogue **3a**, is also indicative in this respect.

The dramatic difference in reactivity of cyclohexyl and benzyl radicals also deserves comment. Both radicals must have comparable adiabatic ionization potentials (cyclopentyl, 7.21 eV (IP for cyclohexyl is not available); benzyl, 7.20 eV).[16]

Therefore, the difference in reactivity is not caused by the difference in the electron donor ability of these two radicals but is most likely due to the difference in bond dissociation energies (BDE) of the carbon–iodine bonds in the respective iodoalkanes (ΔBDE (cy-C$_6$H$_{11}$I – PhCH$_2$I) = 11.5 ± 1.0 kcal/mol).[17]

Preliminary results show that cyclohexyl radicals are also capable of debromination of *o*-bromohexafluorocumyl alcohol (see Table 3).

Further work on these interesting reactions (also involving still some other alkyl radicals) is in progress, and the results of these studies will be reported in due course.

Experimental Section

General Methods. NMR spectra were recorded on a Bruker Avance 300 DPX spectrometer. Chemical shifts are reported relative to internal standards Me$_4$Si or CCl$_3$F. IR spectra were measured on a Perkin-Elmer FTIR 2000 instrument. Melting points are uncorrected. Microanalyses were performed on a Perkin-Elmer 2400 CHN Analyzer. GC analyses were carried out on a Hewlett-Packard 6890 gas chromatograph or GC-MS combination, using 30 m capillary HP5 or Innowax columns. Mass spectra and high resolution mass measurements were performed on a VG-Analytical Autospec EQ instrument.

Materials. Solvents for the decomposition and iodine atom abstraction studies were column distilled before use. THF was freshly distilled from LiAlH$_4$ in an argon atmosphere. In kinetic measurements, deuterated NMR solvents (Fluka), benzene-d_6 (>99.95%D), acetonitrile-d_3 (>99.8%D) and cyclohexane-d_{12} (~99.5%D), were used as received. *tert*-Butyl hydroperoxide was purified by the literature method,[18] di-*tert*-butyl peroxyoxalate (DBPO),[19] dioctanoyl peroxide,[20] 1-chloro-3,3-dimethyl-1*H*-1,2-benziodoxole (**1a**), and 1-chloro-5-methyl-3,3-bis(trifluoromethyl)-1*H*-1,2-benziodoxole (**2c**)[4d,15] as well as alcohols **3a** and **3c**[4d] were prepared according to the literature procedures.

1-*tert*-Butylperoxy-1*H*-1,2-benziodoxoles (2). A Typical Procedure: 1-*tert*-Butylperoxy-3,3-dimethyl-1*H*-1,2-benziodoxole (2a). A mixture of *t*-BuOK (5.0 mmol) and *t*-BuOOH (6.0 mmol) in 10 mL of THF was slowly added to a stirred THF solution of **1a** in an ice bath. The reaction mixture was diluted with diethyl ether–pentane (1:1), washed three times with water, and dried over Na$_2$SO$_4$, the solvent evaporated, and 1.51 g of the crude product was obtained. Recrystallization from hexane yielded 0.88 g (50%) of **2a**, mp 92–95 °C. ^{1}H NMR (CDCl$_3$) δ: 1.29 (s, 9H, *t*-Bu); 1.48 (s, 6H, Me3); 7.18 (dd, *J* = 1.5, 7.4 Hz, 1*H*, H4); 7.44 (dt, *J* = 1.3, 7.3 Hz, 1*H*, H5); 7.50 (dt, *J* = 1.6, 7.6 Hz, 1*H*, H6); 7.94 (dd, *J* = 1.2, 8.0 Hz, 1*H*, H7).

1-*tert*-Butylperoxy-5-methoxy-3,3-dimethyl-1*H*-1,2-benziodoxole (2b). Mp 65–68 °C. ^{1}H NMR (CDCl$_3$) δ: 1.26 (s, 9H, *t*-Bu); 1.46 (s, 6H, Me3); 3.85 (s, 3H, OMe); 6.72 (d, *J* = 2.7 Hz, 1*H*, H4); 7.05 (dd, *J* = 8.9, 2.7 Hz, 1*H*, H6); 7.77 (d, *J* = 9.0 Hz, 1*H*, H7).

1-*tert*-Butylperoxy-5-methyl-3,3-bistrifluoromethyl-1*H*-1,2-benziodoxole (2c). Yield (57%) mp 131–132.5 °C. ^{1}H NMR (CDCl$_3$) δ: 1.29 (s, 9H, *t*-Bu); 2.51 (s, 3H, Me5); 7.50 (bs, 1*H*, H4); 7.58 (d, *J* = 8.5 Hz, 1*H*, H6); 7.92 (d, *J* = 8.4 Hz, 1*H*, H7).

Thermal Decomposition of (*tert*-Butylperoxy)iodanes. A Typical Procedure. **2a** or **2c** (0.05 mmol) was dissolved in 1 mL of the appropriate solvent, and the solution was placed in an ampoule, purged with argon, and sealed. The ampoules were heated in a boiling hexane (69 °C, for **2a**) or cyclohexane (81 °C, for **2c**) bath for 3 and 30 h, respectively. The ampoules were opened, and a weighted amount of bromobenzene as the internal standard was added to the reaction

(12) The strength of the intramolecular hydrogen bonding in *o*-iodophenol was estimated by IR (CCl$_4$) to be 1.55 ± 0.15 kcal/mol (Bourassa-Bataille, H.; Sauvageau, P.; Sandorfy, C. *Can. J. Chem.* **1963**, *41*, 2240. Carlson, G. L.; Fateley, W. G.; Manocha, A. S.; Bentley, F. F. *J. Phys. Chem.* **1972**, *76*, 1553. Theoretical studies have indicated that the intramolecular interactions in the cis conformer of *o*-halophenols are due to a competition between the attractive and repulsive H···halogen interactions, as well as the O···halogen repulsions. An important factor is also the O–H···X angle (Dietrich, S. W.; Jorgensen, E. C.; Kollman, P. A.; Rothenberg, S. *J. Am. Chem. Soc.* **1976**, *98*, 8310). Since this angle is near to 180° in the six-membered hydrogen-bonded ring in *o*-iodocumyl alcohols, i.e., the optimal value for such interactions (it is around 141° in *o*-iodophenol), it seems safe to predict that the strength of the intramolecular hydrogen bonding in these compounds must be ≥2 kcal/mol.

(13) Fukui, K.; Morokuma, K.; Kato, H.; Yonezava, T. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 217. Nagai, S.; Gillbro, T. *J. Phys. Chem.* **1977**, *81*, 1793. Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 185.

(14) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

(15) Moss, R. A.; Wilk, B.; Krogh-Jespersen, K.; Blair, J. T.; Westbrook, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 250.

(16) (a) Hayashibara, K.; Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5441, and references cited therein. (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(17) (a) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; pp. 28–29. (b) *Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Raton, 1995. (c) Denisov, E. T. *Zh. Fiz. Khim.* **1995**, *69*, 436. (d) Prof. S. W. Benson, personal communication.

(18) Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1983**, *48*, 3607.

(19) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

(20) Cooper, W. *J. Chem. Soc.* **1951**, 3106.

(21) Moss, R. A.; Alwis, K. W.; Shin, J. *J. Am. Chem. Soc.* **1984**, *106*, 2651.

(22) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.

mixture, which was subsequently analyzed by GC. The identity of the products was determined by GC-MS and by matching with authentic samples.

Deiodinations by Alkyl Radicals. A Typical Procedure: Substituted iodobenzene (0.10 mmol) and 0.10 mmol of DBPO, together with one drop of bromobenzene (internal standard), were dissolved in 4 mL of deaerated solvent. The solution was heated in an argon atmosphere at 70−80 °C (when in cyclohexane or benzene—under reflux; in the case of isobutane, the reaction mixture was heated in a sealed heavy wall tube) for 2−4 h and analyzed by GC. When radical sources other than DBPO were used, the reaction times were adjusted according to their decomposition rates.

The Reaction of 2-(2-Iodophenyl)-2-propanol with DBPO in Cyclohexane-d_{12}. **3a** (37 mg, 0.14 mmol) and 25 mg (0.11 mmol) of di-*tert*-butyl peroxyoxalate (DBPO) was dissolved in 1 mL of cyclohexane-d_{12} (Fluka, 99.5%D), the solution was flushed with argon, and heated for 2 h under reflux in an argon atmosphere. After chromatography on silica gel with diethyl ether−pentane (1:3) as the eluent, 15 mg of an oily product was isolated. GC analysis showed a pure compound with a retention time identical to that of 2-phenyl-2-propanol. Spectroscopic data correspond to 2-(2-deuterophenyl)-2-propanol: ^{1}H NMR (CDCl$_3$) δ: 1.59 (s, 6H, H1, H3); 1.75 (s, OH); 7.25 (ddd, $J =$ 7.61; 6.93; 1.33 Hz, 1H, H4′); 7.31−7.38 (m, 2H, H3′, H5′); 7.50 (dm, $J =$ 8.5 Hz, 1H, H6′). ^{13}C NMR (CDCl$_3$) δ: 31.77 (C1, C3); 72.53 (C2); 124.08 (t-1:1:1, $^1J_{C-D} =$ 24.0 Hz, C2′); 124.37 (C6′); 126.70 (C4′); 128.12 (C3′); 128.23 (C5′); 149.05 (C1′). MS m/z (%): 137 (M$^+$, 4); 122 (100); 121 (12); 106 (7); 92 (8); 78 (23).

The Reaction of *O*-Deutero-2-(2-iodophenyl)-2-propanol with DBPO in Cyclohexane. The solution of **3a** (0.27 mmol) in 3 mL of degassed cyclohexane and 0.50 mL of deuterium oxide (Fluka, 99.95%D) was irradiated in an ultrasound bath for 30 min, the layers were separated, and the organic layer was dried over Na$_2$SO$_4$. The degree of the isotopic exchange was estimated by ^{1}H NMR to be about 60%. To this solution was added 0.10 mmol of DBPO, and the reaction mixture was heated in an argon atmosphere under reflux for 2 h and analyzed by GC-MS. No incorporation of deuterium into iodocyclohexane or 2-phenyl-2-propanol was found.

The Reaction of 2-(2-Iodophenyl)-2-propanol with Dibenzoyl Peroxide in Benzene. The solution of 0.115 mmol of **3a**, 0.111 mmol of dibenzoyl peroxide, and 0.118 mmol of bromobenzene as the internal standard in benzene was heated for 24 h under reflux in an argon atmosphere. GC analysis showed partial (64%) disappearance of **3a** and the formation of 57% of iodobenzene and 32% of 2-phenyl-2-propanol, together with biphenyl and some benzoic acid. (The discrepancy between the percentage of iodobenzene and 2-phenyl-2-propanol in the reaction mixture is probably due to formation of nonvolatile byproducts.)

Kinetic Measurements. Kinetic measurements were carried out in NMR tubes, flushed with argon, and sealed, in a thermostated probehead of the NMR spectrometer (B = 7 T) or in a water bath thermostat. The temperature in the NMR spectrometer was calibrated by means of the methanol sample. The temperature was held within ±0.1 °C. The integral of H7 was followed usually to 50−70% conversion and compared with a standard, which was an integral of residual protons in the deuterated solvent (benzene and acetonitrile) or the methyl signal of added anisole in cyclohexane. The measurements in the thermostat were carried out by a rapid transfer of the NMR tubes from the thermostat to the NMR probehead, heated to the same temperature. After measurements, the tubes were quickly returned to the water bath. Control experiments with five tubes, containing the aliquots of the same initial solution and taken one by one from the water bath in 30 min intervals, yielded the same result within the experimental error.

Kinetic and activation parameters were obtained by standard procedures.

Relative Rates of Deiodination of Substituted 2-(2-Iodophenyl)-2-propanols by Cyclohexyl Radicals. A solution of substituted 2-(2-iodophenyl)-2-propanol (5-OMe, 5-Me, 5-Cl, and 4-Cl; 0.10 mmol), **3a** (0.10 mmol), and DBPO (0.05 mmol) in 5 mL of cyclohexane was heated under reflux in an inert atmosphere for 2 h and analyzed by GC. The relative rates k_X/k_H were calculated by using the integrated rate equation, $k_X/k_H = \ln[(A - X)/A]/\ln[(B - Y)/B]$, where A is the amount of the substituted alcohol, B is the amount of **3a** at the beginning of the reaction, and X and Y are the amounts of the corresponding deiodinated alcohols at the end of the reaction.

Supporting Information Available: Additional spectroscopic (IR, ^{13}C and ^{19}F NMR, MS) data and elemental analyses of (*tert*-butylperoxy)iodanes **2a**, **2b**, and **2c**, full details of syntheses and characterization data for 1-chloro-5-methoxy-3,3-dimethyl-1*H*-1,2-benziodoxole (**1b**), 2-(2-iodophenyl)-2-methoxypropane, 2-(2-iodo-5-methoxyphenyl)-2-propanol (**3b**), 2-(2-iodo-5-methylphenyl)-2-propanol, 2-(5-chloro-2-iodophenyl)-2-propanol, 2-(4-chloro-2-iodophenyl)-2-propanol, and 2-(2-bromo-5-methylphenyl)-1,1,1,3,3,3-hexafluoro-2-propanol, infrared OH stretching frequencies for selected cumyl alcohols in CCl$_4$ (7 pages). See any current masthead page for ordering and Internet access instructions.

JA9636404