differences. For example, it seems surprising at first sight that the two *ortho* pyridazynes are predicted to differ so much in energy. The difference can, however, be explained at once in terms of PMO theory. Several of the didehydrodiazines are also predicted to undergo ring opening or loss of nitrogen relatively easily, unlike their benzyne analogues. This difference can again be easily explained, being due to the fact that the C≡N and N≡N triple bonds are much stronger than C≡C. Perhaps the most interesting conclusion is that several of the meta and para didehydrodiazines should, like *m*- and *p*-benzyne, be relatively stable species. As yet there is not evidence for the intervention of 1,3- or 1,4-didehydro derivatives of aromatic compounds as reaction intermediates; yet our calcultions suggest that they should often be comparable in stability with their 1,2 counterparts.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. F49620-83-C-0024) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out on a DEC VAX 11-780 computer purchased with funds provided by the National Science Foundation (Grant CHE78-03213) and the University of Texas at Austin.

Registry No. 7, 83421-60-7; **8**, 83421-61-8; **9**, 91202-21-0; **10**, 91202-22-1; **11**, 91202-23-2; **12**, 91202-24-3; **20**, 20722-78-5; **22**, 91202-25-4; **23**, 91202-26-5; **24**, 91202-27-6; **25**, 91202-28-7; **27**, 91202-29-8; **28**, 91202-30-1; **29**, 91202-31-2; **34**, 91202-32-3; **35**, 91202-33-4; **36**, 91202-34-5.

On the Structure of *tert*-Butyl Hypoiodite

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada. *Received November 2, 1983*

Abstract: A compound known as "*tert*-butyl hypoiodite" has hitherto been referred to in the literature as a reagent with some synthetic utility. Three methods of preparation have been used to make this material: the reaction of *tert*-butyl hypochlorite with iodine, the reaction of *tert*-butyl hypochlorite with metal iodides, and the reaction of potassium *tert*-butoxide with iodine. Physical and chemical evidence is offered to show that the reagent obtained from the first of these methods is different from that made from the latter two methods. Reaction schemes are proposed to account for the different properties and reactivities of the two reagents. Structures are proposed for the two reagents which rationalize both the physical and chemical properties of the two materials.

In recent years organic hypoidodites, generated in situ, have found a considerable use in organic synthesis. In particular a reagent which can be formally considered to be "*tert*-butyl hypoiodite" has been used to good effect both as a homolytic and heterocyclic source of iodine. Although its use is well documented, to date no convincing physical evidence has been presented regarding the structure of this compound.

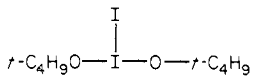
Walling[5] in his studies of the free-radical chlorination reactions of *tert*-butyl hypochlorite observed that iodine, normally a free-radical scavenger, accelerated the reaction. It was evident that *tert*-butyl hypochlorite reacted with iodine to produce a species that reacts faster than *tert*-butyl hypochlorite itself.

Organic hypoiodites first found a synthetic use in steroid chemistry. Barton[6] used "*tert*-butyl hypoiodite" as a reagent to prepare steroid hypoiodites from steroidal alcohols. These were used as intermediates in an intramolecular hydrogen abstraction reaction; i.e., they were photolyzed and underwent a 1,5-carbon to oxygen hydrogen abstraction, followed by iodination and subsequent ring closure of the iodo alcohols. The "*tert*-butyl hypoiodite" was generated by the reaction of potassium *tert*-butoxide with iodine or the reaction of *tert*-butyl hypochlorite and iodine. Barton proposed that the second reaction produced a mixture of *tert*-butyl hypoiodite and iodine monochloride. Similar steroid reactions were extensively studied by Heusler.[7] The "steroid hypoiodites" were generated by using lead tetraacetate and iodine, presumably via the intermediacy of acetyl hypoiodite.

Barton[8] used "*tert*-butyl hypoiodite" to prepare *N*-iodoamides. On photolysis the compounds underwent an intramolecular hydrogen abstraction to give imino lactones which were hydrolyzed to lactones. Again the "*tert*-butyl hypoiodite" was formed from the reaction of *tert*-butoxide or *tert*-butyl hypochlorite with iodine.

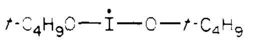
Barton[9] again used "*tert*-butyl hypoiodite" in a "Hunsdieker" type reaction to decarboxylate carboxylic acids. He reported good yields of iodocyclohexane from cyclohexanecarboxylic acid and showed this to be a useful way to synthesize bridgehead iodides.[9,11] Goosen[10] studied this reaction with a range of para substituted phenylacetic acids. He concluded that an acyl hypoiodite was an intermediate and reported a ρ value of -1.09 for its decomposition.

In this laboratory "*tert*-butyl hypoiodite" was generated from *tert*-butyl hypochlorite and mercuric iodide[12] and was used in the free-radical iodination of alkanes. The reaction represented a unique way to carry out this transformation. The substitution proceeded in good yield and with a high selectivity ($k_s/k_p = 29{:}1$).[12] On the basis of the high selectivity it was postulated that the "*tert*-butyl hypoiodite" exists as a 10-I-3 hypervalent species, **1**, and that the hydrogen abstracting species was an 9-I-2 iodonyl radical, **2**.



$$t\text{-}C_4H_9O{-}\overset{\displaystyle I}{\overset{|}{I}}{-}O{-}t\text{-}C_4H_9$$

1



$$t\text{-}C_4H_9O{-}\dot{I}{-}O{-}t\text{-}C_4H_9$$

2

These conclusions are in good accord with similar work that has been done on the selectivity exhibited by an iodonyl radical in this[13-15] and other[16,17] laboratories. Iodine(III) radical species

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have been generally accepted as being highly selective hydrogen abstracting species.

Solutions of "*tert*-butyl hypoiodite" have also been used in heterocyclic reaction systems. The reagent has been used to prepare esters from carboxylic acids and alkyl iodides.[18] Its use in the iodination of some aromatics with strong electron donor substituents has been reported.[19] Recently, it has been used in an addition reaction to olefins which is thought to proceed via a bridged iodonium ion intermediate.[20]

The present study is an attempt to further define the structure of reagent and to compare the composition of the reagent generated by the three methods: the reaction of *tert*-butyl hypochlorite with iodine, the reaction or *tert*-butyl hypochlorite with metal iodides, and the reaction of potassium *tert*-butoxide with iodine.

Results and Discussion

Structure Assignment for "*tert*-Butyl Hypoiodite". The reagent, synthesized by the various methods, was analyzed by a number of techniques.

Spectroscopic methods included visible spectroscopy, high-resolution ^1H and ^{13}C NMR spectroscopy, and infrared spectroscopy (720–250 cm^{-1}).

The average molecular weight of the species in the reagent "*tert*-butyl hypoiodite" was determined from freezing point depression measurements on carbon tetrachloride. In some cases these values were corrected for unreacted materials present in the solutions.

The "*tert*-butyl hypoiodite" prepared by different methods was chemically analyzed by a comparison of its homolytic reaction with cyclohexane and by studying its hydrolysis reactions. The reaction with water was assumed to be similar to that of the iodine(III) compound, $I(OCOR)_3$.[21,22] Hydrolysis of the triacetate follows the stoichiometric relationship shown in eq 1–3.

$$I(OCOR)_3 + 3H_2O \rightarrow [I(OH)_3] + 3RCO_2H \quad (1)$$

$$5[I(OH)_3] \rightarrow 3HIO_3 + I_2 + 6H_2O \quad (2)$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (3)$$

Iodine produced from reaction 2 can be extracted from aqueous solution with carbon tetrachloride and estimated by titration against a standard sodium thiosulfate solution. Similarly, the iodine produced from the reaction of iodate with the acidified iodide solution, reaction 3, can be likewise determined by titration. If the iodine originally exists in oxidation state III, then the ratio of iodine from reactions 3 and 2 is theoretically 9:1. The value for an I(V) species would be 20:1. Iodine monochloride, an I(I) species, reacts with water and produces an iodine ratio of 1.5:1 (see eq 6/5).[23,24]

$$ICl + H_2O \rightarrow IOH + HCl \quad (4)$$

$$5(IOH) \rightarrow HIO_3 + 2I_2 + 2H_2O \quad (5)$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (6)$$

Experimentally determined values were corrected for free iodine or iodine monochloride found to be present by visible spectroscopy.

Table I. High-Resolution NMR Data for "*tert*-Butyl Hypoiodite"

	^{13}C, T = 243 K		
reaction mixture	methyl carbons, ppm	tertiary carbon, ppm	^1H, T = room temp methyl protons, ppm
t-C_4H_9OCl	26.87	83.75	1.36[b]
t-C_4H_9OCl + I_2	30.90	weak signal	
(1:1)[a]	31.12	87.31, 87.50	1.44
(2:1)	30.94	87.87	1.47
(3:1)	30.67, 30.83	86.62, 89.09	1.46
(4:1)	26.63, 30.72, 30.89	85.53, 88.55	1.35, 1.46
a	26.78, 30.95, 31.13	83.29, 85.49, 88.57	
t-C_4H_9OCl + AgI	30.46, 31.18	85.93	1.26[b]
2t-C_4H_9OCl + HgI_2	31.16	85.49	1.26
t-$C_4H_9O^-$ + I_2	31.30	weak signal	1.28

[a] T = room temperature. [b] T = 243 K.

"*tert*-Butyl Hypoiodite" from the Reaction of *tert*-Butyl Hypochlorite and Iodine. Solutions of *tert*-butyl hypochlorite and iodine in carbon tetrachloride were prepared in 1:1, 2:1, 3:1, and 4:1 molar ratios and analyzed by using the techniques described (see Tables I, II, and III).

The color of the solution changed with molar ratio. The 1:1 mixture showed a λ_{max} at 505 nm (cf. iodine in carbon tetrachloride, λ_{max} 520 nm). It is well-known that λ_{max} for iodine shifts to shorter wavelengths in complexing solvents.[25,26] The small shift observed here can readily be explained by a solvent effect due to the "*tert*-butoxy" moiety in the solution. Assuming the extinction coefficient remained constant, then the amount of free iodine in the 1:1 mixture was determined to be approximately 30% of the initial concentration. Similarly, the 2:1 molar mixture showed a λ_{max} in the visible spectrum at 452 nm. This is only a slight shift from λ_{max} for ICl in carbon tetrachloride (460 nm). When the same assumptions were made, the concentration of ICl was approximately 45% of the initial iodine concentration. The 3:1 solution showed a very weak absorption at 450 nm, and the 4:1 solution showed no absorption at all in this region. These results indicate that a 3:1 molar ratio of hypochlorite to iodine gives an almost complete reaction.

The NMR data also indicate that there is a 3:1 stoichiometry (see Table I). The proton NMR spectrum shows a downfield singlet, δ 1.45 ($\pm$0.02) for all the solutions. This is in contrast to the *tert*-butyl singlet, δ1.36, for *tert*-butyl hypochlorite. The absorption at δ 1.36 appears only in the 4:1 mixture, presumably due to excess hypochlorite being present. The carbon-13 NMR spectra confirm this conclusion and give some additional information about the structure of the species present. The methyl carbons in *tert*-butyl hypochlorite give a signal at 26.9 ppm downfield from Me_4Si while all of the hypochlorite/iodine mixtures show signals at about 30.8 ppm. Again only in the 4:1 molar mixture does the absorption of the *tert*-butyl hypochlorite (at 26.8 ppm) appear in addition to the absorption at about 30.8 ppm. In the 3:1 and 4:1 solutions the lower field absorption consists of at least two signals attributable to methyl groups in different magnetic environments.

The infrared spectra for all the *tert*-butyl hypochlorite/iodine mixtures, in the region 240–720 cm^{-1}, show strong absorptions for all the solutions at around 602 and 283 cm^{-1} (see Table II). The absorption at 602 cm^{-1} can be assigned to an O–I stretching

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Table II. IR Spectral Data (240–720 cm^{-1}) for "*tert*-Butyl Hypoiodite" and Related Compounds in CCl_4

	IR absorption bands[a]								
reaction mixture	260–340 cm^{-1} (I–Cl stretch)			340–500 cm^{-1}			500–720 cm^{-1} (I–O stretch)		
$t\text{-}C_4H_9OH$				346 (w)	426 (w)	466 (m)			
$t\text{-}C_4H_9OCl$				355 (m)	428 (w)	466 (m)	536 (m)		
$t\text{-}C_4H_9OCl$				345 (m), 375 (s), 398 (w), 455 (m)					692 (s)
$t\text{-}C_4H_9OCl + I_2$									
(1:1)	283 (s)		340 (s)	355 (sh)	385 (m)	468 (m)		604 (s)	
(2:1)	285 (s)		338 (s)	355 (sh)	385 (m)	469 (m)		604 (s)	
(3:1)	265–308 (s)			350–360 (w)	384 (m)	469 (m)		600 (s)	
(4:1)	280 (s)	300 (sh)		348–360 (w)	384 (m)	469 (m)		600 (s)	692 (w)
$t\text{-}C_4H_9OCl + AgI$	283 (w)			347 (w)	382 (m)	458 (m)		603 (s)	
$t\text{-}C_4H_9OCl + HgI_2$	280 (w)			347 (w)	382 (m)	458 (m)		602 (s)	
$t\text{-}C_4H_9O^- + I_2$				346 (w)	382 (m)	459 (m)		603 (s)	
$PhICl_2$[b]	250 (s)	278 (s)				454 (m)			
$PhICl(OC_4H_9)$[c]		290 (s)				454 (m)	590 (m)	600 (w)	655 (m) 670 (m) 680 (m)

[a] w = Weak, m = medium, s = strong, sh = shoulder. [b] Nujol mull using CsI plates: 220–600 cm^{-1}. [c] Nujol mull using CsBr plates: 240–720 cm^{-1}.

Table III. Visible Spectra, Average Molecular Weights, and Titrimetric Data for *tert*-Butyl Hypoiodite

reaction mixture	visible spectrum		av M_r of[a] species present	hydrolysis[a] ratios
	color	λ_{max}, nm		
$t\text{-}C_4H_9OCl$	yellow-green			
$t\text{-}C_4H_9OCl + I_2$	red-purple	505	480	2.2
$2t\text{-}C_4H_9OCl + I_2$	orange	452	516	7.6
$3t\text{-}C_4H_9OCl + I_2$	yellow	452 (vw)	510	9.5 (±0.1)
$4t\text{-}C_4H_9OCl + I_2$	yellow-green			15.1 (±0.5)
$t\text{-}C_4H_9OCl + AgI$	red-orange	515	364 (±43)[b]	2.5 (±0.7)
$2t\text{-}C_4H_9OCl + HgI_2$	red-orange	515	337 (±55)	3.5 (±0.6)
$t\text{-}C_4H_9O^- + I_2$	red-orange	515	288 (±40)	

[a] Values have been corrected for the free iodine present. [b] Average value from two determinations.

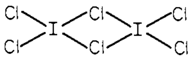
mode. The comparable O–Cl stretching mode absorption in *tert*-butyl hypochlorite is at 692 cm^{-1}.[27] In the 4:1 mixture this absorption appears in addition to the signal at 602 cm^{-1}, indicating the presence of excess hypochlorite. The stretching vibration for I–Cl in carbon tetrachloride is at 375 cm^{-1} but shifts to lower wavenumbers in complexing solvents.[28,29] In the reaction mixtures, the absorptions at around 280 cm^{-1} are assigned to an I–Cl bond. The three absorptions in the 340–500-cm^{-1} region are also present in the spectra of *tert*-butyl alcohol, *tert*-butyl hypochlorite, and di-*tert*-butyl peroxide. They have not been further assigned.

The molecular weight determinations for the 1:1, 2:1, and 3:1 hypochlorite/iodine mixture indicate that the average molecular weight of the species present, after correcting for free iodine or iodine monochloride present, is approximately 500 (see Table III).

The iodine ratios from the hydrolysis reaction increase with the amount of hypochlorite added. The 3:1 molar mixture of hypochlorite and iodine shows a ratio of 9.5:1, almost exactly the 9:1 ratio theoretically expected for a trivalent iodine species.

The results indicate that the 3:1 solution represents situation of complete reaction. Before proposing possible structures of the reagent the following information must be accounted for: (a) the 3:1 mole ratio of the reactnats, (b) the presence of iodine(III) species, (c) the presence of both O–I and I–Cl stretching modes in the IR spectrum, (d) the molecular weight of approximately 500, and (e) the appearance of two methyl carbon absorptions close together in the carbon-13 NMR spectrum.

It is known that iodine trichloride exists in the solid state as a flat dimer, I_2Cl_6 (see structure **3**).[30,31] In solution it dissociates into iodine monochloride and chlorine[31,32] with the expected absorption maxima at 460 and 332 nm in the UV–visible spectrum. The 3:1 solution showed only a trace of absorption in the same region. For this reason, both iodine trichloride and iodine monochloride can be ruled out as important components of the 3:1 solution.



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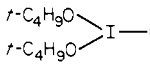
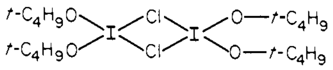


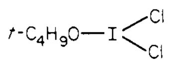
4

(M_r 309)



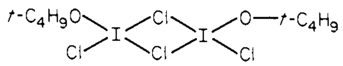
5

(M_r 617)



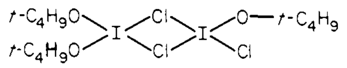
6

(M_r 271)



7

(M_r 542)



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(M_r 580)

A sequence of reactions can be envisaged which rationalizes the formation of several trivalent iodine species (see Scheme I). The overall rection produces species **4** and **6** which are both trivalent iodine species containing O–I and I–Cl bonds.

However, bridged chlorine structures analogous to I_2Cl_6 can be proposed to explain the molecular weight of the 3:1 molar reaction (see structures **4**–**8**). The molecular weights of approximately 500 strongly suggest that species **4** and **6** are in dynamic equilibrium with their dimers: species **5**, **7**, and **8**. The average molecular weight of the species present in such an

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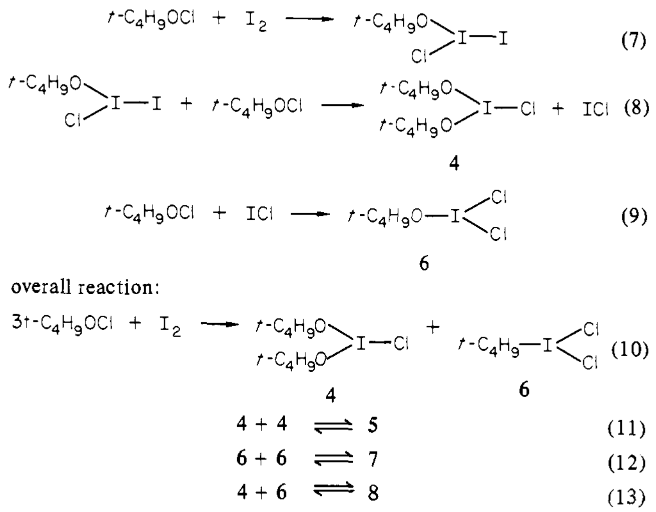
Scheme I



$$4 + 4 \rightleftharpoons 5 \quad (11)$$

$$6 + 6 \rightleftharpoons 7 \quad (12)$$

$$4 + 6 \rightleftharpoons 8 \quad (13)$$

equilibrium would account for the observed values. It is encouraging to note that as the ratio of hypochlorite/iodine increases the observed average molecular weight also increases. This observation is consistent with the proposed reaction scheme, since the concentration of bridged chlorine dimers (structures **5**, **7**, and **8**) would be expected to increase as more trivalent iodine compounds are formed.

The suggested existence of the chlorine-bridged dimers is based solely on the data obtained from the molecular weight determinations. These experiments were done at approximately −23 °C, and it is recognized that at room temperature the equilibrium may change and species **4** and **6** may dominate.

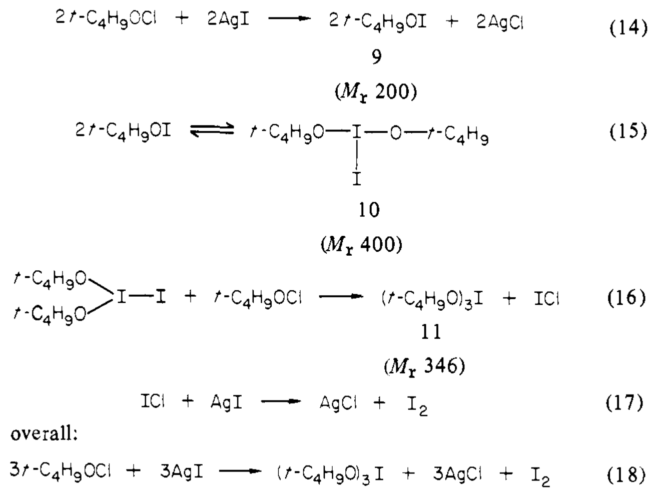
tert-Butoxy moieties in the dimers are in either one of two environments, i.e., geminal to a chlorine atom or geminal to another *tert*-butoxy group. The methyl carbons can be anticipated to be in slightly different magnetic environments, and, indeed, two absorptions are observed in the carbon-13 NMR spectrum. In the 4:1 hypochlorite/iodine solution the ratio of protons from the iodine species to those from excess *tert*-butyl hypochlorite was found from integrating the signals in the proton NMR spectrum to be 6.1:1. They suggested that some of the hypochlorite must be reacting further. The suggestion was confirmed when the hydrolysis ratio for the 4:1 mixture was determined to be 15.1:1 (see Table III). Such a high iodine ratio requires that some pentavalent iodine species are present, although this aspect was not further studied.

"*tert*-Butyl Hypoiodite" from the Reaction of *tert*-Butyl Hypochlorite and Metal Iodide. The reaction of *tert*-butyl hypochlorite with mercuric or silver iodide produces a red-orange solution which forms a gelatinous precipitate upon standing for a few hours. The amount of free iodine present in freshly prepared solutions, as estimated by visible spectroscopy, can vary from almost nothing to approximately 20% of the total iodine content. Both solutions show a λ_{max} at 515 nm which corresponds to the absorption for iodine.

The proton NMR spectra show a singlet at δ 1.26 (see Table I). This can be compared to the methyl singlet at δ 1.36 for *tert*-butyl hypochlorite and a singlet at δ 1.45 for the hypochlorite–iodine solutions. Similarly, the carbon-13 NMR spectra show signals at different shifts for both the methyl and *tert*-butoxy carbon atoms compared to the comparable shifts for *tert*-butyl hypochlorite. These results indicate that the reagent produced from this reaction is different from that of the reaction of *tert*-butyl hypochlorite and iodine.

The strong absorptions at 602 cm^{-1} in the IR spectra for the two solutions can be assigned to an O–I stretching mode (see Table II). The weak signals at 280 cm^{-1} are proably due to an I–Cl stretching mode which arises from a small amount of reaction of *tert*-butyl hypochlorite with liberated iodine. The absorptions in the 340–500-cm^{-1} region are again found in related compounds and have not been further assigned.

Scheme II



$$2\,t\text{-}C_4H_9OCl + 2AgI \longrightarrow 2\,t\text{-}C_4H_9OI + 2AgCl \quad (14)$$

$$ICl + AgI \longrightarrow AgCl + I_2 \quad (17)$$

$$3\,t\text{-}C_4H_9OCl + 3AgI \longrightarrow (t\text{-}C_4H_9O)_3I + 3AgCl + I_2 \quad (18)$$

Molecular weight measurements show that the reagent produced from *tert*-butyl hypochlorite reacting with silver or mercuric iodide have similar molecular weight, i.e., approximately 350 (see Table III).

The iodine ratios from the hydrolysis reactions are in reasonable agreement for both methods of preparation. The values of 2.5:1 and 3.5:1 are consistenly in excess of the 1.5:1 ratio theoretically expected for a monovalent iodine species. The results of the hydrolysis, however, indicate a mixture of monovalent and trivalent species.

It can be concluded that the reaction of *tert*-butyl hypochlorite with the two metal iodides, mercuric or silver iodide, produces the same material. Because the respective metal chloride can be isolated in almost quantitative yield, the overall stoichiometlry of the reaction must be

$$n\text{-}C_4H_9OCl + MI_n \rightarrow \text{“}n\text{-}C_4H_9OI\text{”} + MCl_n$$

However, the variable amounts of free iodine produced from reaction to reaction, as well the intermediate hydrolytic behavior and molecular weight, suggests that a more complex scheme is involved, one which still follows a 1:1 stoichiometry, but will likewise accomodate the production of free iodine. Scheme II can be suggested as fulfilling these requirements.

In the mechanism, two competing pathways control the amount of free iodine produced. When the reaction follows the straight forward sequence outlined by eq 14 and 15, an equilibrium between species **9** and **10** is set up. Species **9** has a molecular weight of 200, and as it is in oxidation state I the hydrolysis ratio from this species can be anticipated to be 1.5:1. Similarly, species **10** has a molecular weight of 400 and as it is in a mixed I and III oxidation state the hydrolysis ratio can be anticipated to be 5.3:1. Thus, if an equilibrium exists, intermediate values of molecular weight and hydrolysis ratios can be expected. The scheme incorporates a further set of reactions to explain the production of varying amounts of molecular iodine, eq 16 and 17. Dimeric "*tert*-butyl hypoiodite" reacts with *tert*-butyl hypochlorite to form species **11** which has a molecular weight of 346 and an oxidation state of III (see eq 16). The iodine monochloride produced reacts with silver iodide to silver chloride and free iodine (eq 17). The proposal that the reaction of iodine monochloride and silver iodide produced molecular iodine was confirmed when equimolar amounts of iodine monochloride and silver iodide were found to react, and silver chloride was recovered in quantitative yield. The variable amounts of free iodine produced during the reaction of *tert*-butyl hypochlorite and metal iodide are speculatively suggested as being due to the nonhomogeneous nature of the reaction. Physical factors such as speed of mixing and particle size of the metal iodide may well play a role in determining the choice of reaction paths.

"*tert*-Butyl Hypoiodite" from the Reaction of Potassium *tert*-Butoxide and Iodine. The reaction of potassium *tert*-butoxide and iodine, in carbon tetrachloride, produces upon filtration a red-

Table IV. Photoinitiated Reaction of *tert*-Butyl Hypoiodite with Cyclohexane (40 °C)

product	t-C_4H_9OCl + AgI[a]	2(t-C_4H_9OCl) + HgI_2[a]	t-$C_4H_9O^-$ + I_2[b]
t-C_4H_9OH	0.99	0.97	1.14
$C_6H_{11}Cl$	0.03	0.03	
$C_6H_{11}I$	0.87	0.86	0.74
trans-$C_6H_{10}Cl_2$	trace	trace	
trans-$C_6H_{10}ClI$	0.02	0.02	
I_2	0.01	trace	0.21

[a] Mol/Mol *tert*-butyl hypochlorite. [b] Mol/mol active halogen equivalent as determined by titration with standard thiosulfate.

Table V. Photoinitiated Decomposition of *tert*-Butyl Hypoiodite, from the Reaction of *tert*-Butyl Hypochlorite with Mercuric Iodide, in CCl_4 at 40 °C

product	yield[a]	yield[b]
acetone	55.0	55.0
iodomethane	55.0	not measured
tert-butyl alcohol	25.0	21.0
1-iodo-2-methyl propanol	2.3	11.0
isobutylene oxide	3.3	4.4
1-iodo-2-propanone	3.0	15.0
iodine	11.0	not measured

[a] (Mol/mol "*tert*-butyl hypoiodite") × 100. [b] Yields of analogous chloro compounds from the photoinitiated decomposition of *tert*-butyl hypochlorite.[35]

Table VI. Reaction of *tert*-Butyl Hypoiodite, from the Reaction of *tert*-Butyl Hypochlorite with Mercuric Iodide, with Hydrocarbons at 47 °C[a]

hydrocarbon	product	yield,[b] %
neopentane	neopentyl iodide	28 (34)
n-butane	2-iodobutane (95 ± 3%) 1-iodobutane (5 ± 3%)	35 (39)
cyclohexane	cyclohexyl iodide	51 (60) (70[c])
isobutane	isobutyl iodide	(<2)
	tert-butyl iodide	(<2)
toluene	benzyl iodide	34 (38)

[a] Reactions were run in Freon 113 solutions, 1.0–1.2 M in *tert*-butyl hypoiodite and 3.8–4.2 M in hydrocarbon. [b] Values reported were based on the initial concentration of *tert*-butyl hypochlorite used and represent yields of pure product isolated from the reaction by distillation. Values in parentheses were determined by GLPC. [c] Yield obtained with carbon tetrachloride solution 0.133 M in *tert*-butyl hypoiodite and 2.47 M in cyclohexane at 40 °C.

Table VII. Relative Reactivities of Alkyl Iodides and Cyclohexane toward *tert*-Butyl Hypoiodite, made from *tert*-Butyl Hypochlorite and Mercuric Iodide, at 40 °C[a]

substrate	relative reactivity per molecule
cyclohexane	1.00
tert-butyl iodide	5.60
2-iodobutane	0.76
isobutyl iodide	0.61

[a] The reactions were run in Freon 113 solutions 0.133 M in *tert*-butyl hypoiodite and 0.270 M in substrate.

orange solution which also forms a gelatinous precipitate on standing. This material is visibly similar to the product of the reaction of *tert*-butyl hypochlorite and the metal iodide in carbon tetrachloride. It shows a λ_{max} at 515 nm in the visible spectrum and the free iodine was determined to be approximately 10% of the total iodine content. Material produced from both methods show similar proton and carbon-13 NMR spectra (see Table I). The IR spectrum shows the same absorptions without, of course, the weak I–Cl absorption in the 260–340-cm^{-1} region (see Table II). The average molecular weight is, within experimental error, similar to that for the metal iodide reaction (see Table III). The hydrolysis ratios were measured for this reagent but were shown to be invalid, since small amounts of potassium iodide, a reaction product, reacted with iodic acid to release iodine during the initial hydrolysis reaction (see reactions 2 and 3).

However, when the reagent was photolyzed in the presence of *n*-butane, 2-iodobutane and 1-iodobutane were formed. The ratio of the products was found to be 15:1, giving a selectivity primary:secondary (per H) of 22:1. The selectivity compares well with the value of 29:1 found for the reagent prepared from *tert*-butyl hypochlorite and metal iodide (see Table V).

Reactivity of *tert*-Butyl Hypoiodite. Reactions with Cyclohexane. It can be concluded from the structural information that the material derived from the reaction of *tert*-butyl hypochlorite and metal iodide is the same compound but is different from the reagent derived from *tert*-butyl hypochlorite and iodine. The conclusions are substantiated by the results of the reagents' reactions toward cyclohexane. The material derived from metal iodide and hypochlorite reacts, upon photolysis, with cyclohexane to yield iodocyclohexane in good yield (see Table IV). Traces of chlorinated cyclohexane derivatives are observed. The chlorinated cyclohexanes are most likely produced by the reaction of traces of the reagent formed from *tert*-butyl hypochlorite and free iodine, since this reagent has been shown to react photolytically with cyclohexane to produce iodocyclohexane, chlorocyclohexane, *trans*-1,2-dichlorocyclohexane, and *trans*-1-iodo-2-chlorocyclohexane.[33,34] This reaction initially proceeds via a radical mechanism followed, apparently, by subsequent ionic reactions. The material made from the reaction of potassium *tert*-butoxide and iodine also reacts, upon photolysis, with cyclohexlane to produce iodocyclohexane in good yield (see Table IV). Naturally, in this case, traces of chlorinated compounds are not observed.

Photodecomposition of *tert*-Butyl Hypoiodite. A carbon tetrachloride solution of the red-orange reagent derived from hypochlorite and metal iodide was photolyzed at 40 °C for over 2 days (see Table V). The products and their yields are compared to those reported by Walling in his study of the photodecomposition of *tert*-butyl hypochlorite, carried out under similar conditions.[35] The two sets of data are in excellent agreement: analogous decomposition products are produced in essentially similar yields. The higher yields of 1-chloro-methylpropanol and 1-chloro-2-propanone from the hypochlorite decomposition are undoubtedly due to the high reactivity of the chlorine atoms produced in the initial photolysis. Iodine atoms similarly produced from hypoiodite decomposition are unreactive and combine to form molecular iodine which remains in solution. These results indicate that the reagent resulting from the reaction of *tert*-butyl hypochlorite and metal iodide can be empirically considered analogous to *tert*-butyl hypochlorite. This red-orange colored reagent can be appropriately named *tert*-butyl hypoiodite.

Reactions with Other Substrates. Preparatively useful yields of alkyl iodides can be obtained from alkanes using the photolytic reaction of *tert*-butyl hypoiodite (see Table VI). While primary and secondary hydrogens underwent substitution, the iodination failed to produce iodination products with compounds containing tertiary hydrogens. When the reaction with isobutane was run with initially added *tert*-butyl iodide, the iodide was found to react more rapidly than the hydrocarbon substrate. The high reactivity of the tertiary halide clearly explains the absence of alkyl iodides in the reaction of substrates containing a tertiary hydrogen. The tertiary iodides must be formed rapidly: however, they are consumed subsequent to their formation faster than the unreacted substrate (see Table VII).

The high selectivity in the iodination of *n*-butane, primary: secondary (per H) 1:29, as compared to 1:8 for the *tert*-butoxy radical,[5] led to the proposal of the following radical chain process for the reaction, where the iodonyl radical is the abstracting species:[12]

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(33) Unpublished results from this laboratory.

(34) Rowe, J. E. Ph.D. Thesis, University of Alberta, 1974.

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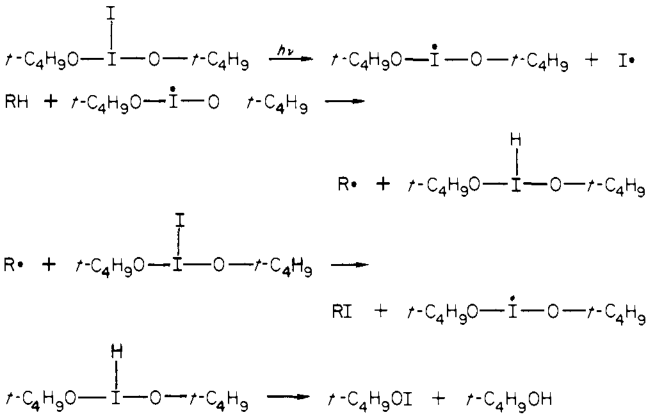

It is known that photolytic reactions with *tert*-butyl hypochlorite can proceed by a mixed chain reaction with the *tert*-butoxy radical and the chlorine atom being the abstracting species.[36] In the present case, iodine atoms are not sufficiently reactive to abstract hydrogen. However, a mixed chain reaction is still possible since structural data suggest that *tert*-butyl hypoiodite has monomeric, structure **9**, and dimeric, structure **10**, species present in solution. Photolysis of these two species can form two radicals capable of hydrogen abstraction: the *tert*-butoxy radical and the 9-I-2 iodonyl radical. The high selectivity observed for this reagent is reminiscent of that observed in the abstraction reactions of other 9-I-2 radicals, Ph–İ–Cl, (primary:secondary reactivity 1:21)[12] and Ph–İ–O–*tert*-C_4H_9 (primary:secondary reactivity ≥ 1:13).[16] The similarity in selectivity is suggestive of the reaction of a 9-I-2 iodonyl radical playing an important role in the reaction but rules out the *tert*-butoxy radical as the sole abstracting species.

Experimental Section

Materials. Iodine and iodine monochloride (BDH Ltd., laboratory reagents) were used as supplied.

Carbon tetrachloride (Fischer Scientific Co., "Spectranalyzed" Reagent) was distilled from phosphorus pentoxide. No impurities were detected by GLPC.

Cyclohexane (Phillips pure or research grade) was used as supplied.

Bromocyclohexane, *trans*-1,2-dichlorocyclohexane (Aldrich), and iodocyclohexane (Eastman Organic Chemicals) were distilled prior to use.

trans-1-Chloro-2-iodocyclohexane was prepared by the procedure of Birckenbach and Goubeau[37] by the reaction of iodine and a slight excess of cuprous chloride with a large excess of cyclohexane in anhydrous ether. The product was obtained in 80% yield, bp 50 °C with (0.8 mm) (lit.[34] 11m °C (14 mm)). The NMR spectral data were identical with the data for *trans*-1-chloro-2-iodocyclohexane published by Premuzic and Reeves.[38]

tert-Butyl hypochlorite was prepared by the method of Teeter and Bell.[39] It was distilled and had bp 70 °C (700 mm) (lit. 77–78 °C (760 mm)). The purity was checked by iodometric titration with thiosulfate solution prior to use (99–100% pure).

Mercuric iodide (BDH Ltd.) was used as supplied.

Silver iodide was prepared by mixing equimolar silver nitrate and potassium iodide solutions. The resulting precipitate was filtered in the absence of strong light, thoroughly washed, and dried in a darkened desiccator.

Potassium *tert*-butoxide was prepared by adding potassium metal to an excess of dry *tert*-butyl alcohol. The mixture was heated under reflux, under a nitrogen atmosphere, until all the potassium had dissolved. The excess *tert*-butyl alcohol was removed by vacuum distillation leaving a colorless solid which has been shown to be a 1:1 complex of potassium *tert*-butoxide and *tert*-butyl alcohol.[40] Pure potassium *tert*-butoxide was prepared by sublimation (170 °C (0.01 mm)) of this crude product (lit.[41] 200 °C (1 mm)).

Analytical Techniques. NMR spectra, both proton and carbon-13, were recorded on a Brucker WH/400 400-MHz spectrometer. The IR spectra in the region 250–720 cm^{-1} were recorded on either a Beckman Model 11 spectrophotometer or a Nicolet Fourier transform spectrophotometer using cesium bromide cells in both cases. Visible spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer or a Pye-Unicam SP1800 spectrophotometer.

The average molecular weights of the species present were determined by the freezing point depression of a carbon tetrachloride solution by using equation

$$M = 1000(gK_f/G\Delta T_f)$$

M is the molecular weight of the solute, ΔT_f is the difference between the freezing point of the solvent and a solution prepared by dissolving g grams of solute in G grams of the solvent, K_f is the freezing point depression constant for the solvent (29.8 deg m^{-1} for carbon tetrachloride[42]). The freezing point was determined by slowly cooling a 0.04 m solution and measuring the temperature fall with a Hewlett-Packard 2801A quartz thermometer. A sharp change in the rate of cooling from a cooling curve, obtained from a plot of temperature vs. time, was taken as the freezing point of the solution. The concentration of free iodine was determined by visible spectrometry, and the molecular weight values were adjusted accordingly.

The total iodine content of the reagent was determined by adding an acidified potassium iodide solution to a known aliquot of "*tert*-butyl hypoiodite" and titrating the iodine released with a standard sodium thiosulfate solution.

Samples of the reagent were hydrolyzed in a separatory funnel. The iodine released was extracted from the aqueous layer 3 times with carbon tetrachloride, and the organic solution was then titrated with standard thiosulfate solution to determine the iodine content. The aqueous layer remaining was treated with an acidified solution of potassium iodide and the iodine released was similarly titrated with thiosulfate solution. The ratio of the titres obtained gave the iodine ratio for the reagent. The concentration of free iodine was determined by visible spectrometry, and the ratio values were adjusted accordingly. In another experiment the water was removed by vacuum distillation and the resulting white solid analyzed by IR spectroscopy. Its spectrum (KBr disk) was found to be identical with the spectrum obtained from authentic iodic acid.

The yields of products analyzed by GIPC were determined by using standard calibration curves constructed from mixture of the added standard and the authentic materials.

Preparation of the Reagent. *tert*-Butyl Hypochlorite and Iodine. The solutions of *tert*-butyl hypochlorite and iodine, of varying molar ratios, in carbon tetrachloride were prepared in a drybox. For example, *tert*-butyl hypochlorite (2.23 g, 2.04 × 10^{-2} mol) was weighed into a 10-mL volumetric flask and made up to the mark with dry carbon tetrachloride. Aliquots of this stock solution was added to the required amount of iodine in 5-mL volumetric flasks. The resulting solutions were shielded from the light and vigorously shaken for 30 min. Carbon tetrachloride was then added to fill the flask to the mark.

***tert*-Butyl Hypochlorite and Metal Iodide.** *tert*-Butyl hypochlorite (0.01 mol) in carbon tetrachloride (6 mL) was added dropwise over 60 min to a suspension of the required amount of metal iodide in carbon tetrachloride (10 mL). The mixture was agitated by the flow of dry nitrogen. The reaction mixture was kept at 0 °C. The resulting red-orange solution was filtered through a sintered glass funnel to remove the metal halides.

The composition of the residual halides was determined by the method of Bekk.[43] Almost quantitative amounts of mercuric or silver chlorides were recovered.

Potassium *tert*-Butoxide and Iodine. In a drybox, freshly sublimed potassium *tert*-butoxide (0.24 g, 2.1 × 10^{-3} mol) was allowed to react with iodine (0.50 g, 2.0 × 10^{-3} mol) in dry carbon tetrachloride (4 mL). The suspension was shaken for 2 h at room temperature. The resulting mixture was filtered through a sintered glass funnel to remove the solid potassium iodide and unreacted potassium *tert*-butoxide. The results was a red-orange solution.

Reactions of *tert*-Butyl Hypoiodite. Photoinitiated Reaction with Cyclohexane. The reagents prepared from hypochlorite and metal iodide or *tert*-butoxide and iodine (1.2 × 10^{-3} mol) were each added to cyclohexane (2 mL) in a glass ampule. The reaction mixture was degassed 3 times by a freeze–thaw method and then sealed under vacuum. The mixtures were allowed to equilibrate at 40 °C and irradiated with two 200-W tungsten lamps for 8 h. The products were analyzed by GLPC lj(6 ft × $^1/_4$ in. 10% DEGS on Chromosorb P-AW, glass column) using bromocyclohexane as an external standard. The products were identified by comparing their retention times with those of the authentic com-

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pounds. Results are summarized in Table IV.

Photodecomposition of *tert*-Butyl Hypoiodite. A solution of the reagent (0.2 M) prepared from the reaction of *tert*-butyl hypochlorite and mercuric iodide was irradiated with a 200-W tungsten lamp for 52 h. The products were separated by preparative GLPC (10 ft × $^1/_4$ in. 10% SE-30, 60/80 Chromosorb W) and the compounds analyzed by NMR. The results are shown in Table V. The product yields were determined by using bromocyclohexane as an added external standard.

Photoinitiated Reactions with Hydrocarbons. Preparative reactions were run in Freon 113 solutions 1.0–1.2 M in *tert*-butyl hypoiodite and 3.8–4.2 M in hydrocarbon and photolyzed at 47 °C for 8 h. The products were characterized by comparison of their IR and NMR spectra and GLPC retention times with those of authentic samples. GLPC analysis was carried out on a 10 ft × $^1/_4$ in. SE 30 on Chromosorb PAW glass column using Freon 112 as an internal standard. Results are summarized in Table VI.

Competitive Reactions of Alkyl Iodides and Cyclohexane. The competitive reactions were run in Freon 113 solutions 0.133 M in *tert*-butyl hypoiodite and 0.270 M in substrate. The ratio of alkyl iodide to cyclohexane was determined by GLPC (25 ft × $^1/_8$ in. Ucon Polar column using Freon 112 as an internal standard) before and after photoinitiated reaction at 40 °C for 15 min. The relative reactivities of alkyl iodides and cyclohexane were thereby determined (see Table VII).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for their generous support of this work.

Registry No. 4, 91083-56-6; **5**, 91083-61-3; **6**, 91083-57-7; **7**, 91083-62-4; **8**, 91083-63-5; **9**, 917-97-5; **10**, 91083-58-8; **11**, 91083-59-9; *t*-C_4H_9OCl, 507-40-4; I_2, 7553-56-2; AgI, 7783-96-2; HgI_2, 7774-29-0; $C_6H_{11}Cl$, 542-18-7; $C_6H_{11}I$, 626-62-0; *trans*-$C_6H_{10}Cl_2$-1,2, 822-86-6; *trans*-$C_6H_{10}ClI$-1,2, 33427-17-7; *t*-C_4H_9OH, 75-65-0; potassium *tert*-butoxide, 865-47-4; cyclohexane, 110-82-7; acetone, 67-64-1; iodomethane, 74-88-4; 1-iodo-2-methylpropanol, 91083-60-2; isobutylene oxide, 558-30-5; 1-iodo-2-propanone, 3019-04-3; neopentane, 463-82-1; *n*-butane, 106-97-8; isobutane, 75-28-5; toluene, 108-88-3; neopentyl iodide, 15501-33-4; 2-iodobutane, 513-48-4; 1-iodobutane, 542-69-8; isobutyl iodide, 513-38-2; *tert*-butyl iodide, 558-17-8; benzyl iodide, 620-05-3.

Characterization of Regiospecific A,C- and A,D-Disulfonate Capping of β-Cyclodextrin. Capping as an Efficient Production Technique[†]

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Abstract: The fundamental aspects underlying the regioselective capping reaction of β-cyclodextrin (hereafter abbreviated as β-CD) were studied, using a series of rigid, aromatic disulfonyl chlorides $ClSO_2XSO_2Cl$ (**2**) (**2a–f**, X = 1,1′-methylenebis(benzene)-4,4′-, 1,1′-oxybis(benzene)-4,4′-, benzophenone-3,3′-, *N*-methylcarbazole-3,6-, biphenyl-4,4′-, and *trans*-stilbene-4,4′-disulfonyl chloride, respectively). A new and convenient method of analysis of regiochemistry has been developed in which the product mixture of each capping was directly converted to the corresponding regioisomeric bis(sulfides), A,B-, A,C-, and A,D-β-CD(SPh-*t*-Bu)$_2$, by treatment with NaSPh-*t*-Bu, and the regioisomer ratio was determined by HPLC. The observed "overall" regiochemistry for all of the capping reagents, except *trans*-stilbene (**2f**), was insensitive to concentration, thus capping seems very attractive as a versatile method, since a high-dilution technique is not necessary and, therefore, cap preparation in large quantities is feasible. On the basis of the concentration-insensitive regiochemistry, *intramolecular capping* (looper's walk) was shown to be much more effective than intermolecular oligomerization. Highly regioselective capping was found in benzophenone-3,3′-disulfonyl chloride (**2c**), which gave mostly A,C regioisomer, while *trans*-stilbene-4,4′- (**2f**) and biphenyl-4,4′-sulfonyl chloride (**2e**) led to almost regiospecific A,D capping.

In cyclodextrin chemistry, considerable attention has been focused on developing techniques to modify primary[1] or secondary hydroxyl group(s).[2] Since 1976, when the first rigid cap (diphenylmethane-capped β-CD, **3a**) was reported by the authors,[3] disulfonate rigid capping has been successfully utilized to difunctionalize cyclodextrin's primary rim[4] for the preparation of sophisticated inclusion hosts[3,4,5a] or enzyme models.[4b,c,5b,c] This concept is also applied to host–guest energy transfer.[6]

Table I. Preparation of Capped β-Cyclodextrin Purified after Discarding Less Soluble Materials

capping reagent, M	β-CD, M	°C	h	yield, %	ref
2a, 6.0 × 10^{-2}	5.0 × 10^{-2}	50	2.5	35	4a
2c, 3.6 × 10^{-2}	3.5 × 10^{-2}	60	1	40	7a
2f, 1.8 × 10^{-2}	1.8 × 10^{-2}	60	1	20	7a,b

The first transannular capping using diphenylmethane-4,4′-disulfonyl chloride **2a** was not regiospecific, but instead gave regioisomers A,C and A,D[4a] (see Scheme I). This unique type of regiochemistry on CD is of considerable interest and, therefore, was investigated further by the authors.[7] Nearly exclusive selection of A,C- and A,D-disulfonate capping was achieved by using benzophenone-3,3′-disulfonyl chloride **2c** and *trans*-stilbene-4,4′-disulfonyl chloride **2f**, respectively. Therefore, the dramatic structural dependence in regioselectivity presents an interesting problem, that is, how the second transannular functionalization can be achieved at the best-fit position (*looper*'s *walk*). The

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[†] Sample of A,C- or A,D-β-CD(SPh-*t*-Bu)$_2$ for a HPLC standard will be given on request.

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