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Oxidation of Benzyltrialkylstannanes by Iodosylbenzene Catalyzed by Iron Tetrakis(pentafluorophenyl)porphyrin Chloride. Possible Role of Benzyloxy Radicals[†]

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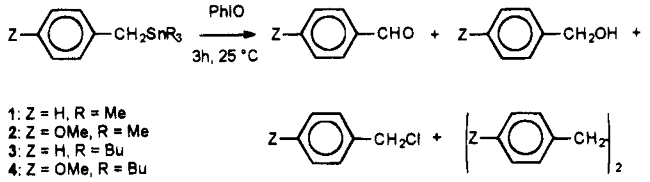
The oxidations of some benzyltrialkylstannanes by iodosylbenzene induced by tetrakis(pentafluorophenyl)porphyrin chloride (TPFP)FeCl have been investigated. Benzaldehydes and benzyl alcohols are the main reaction products, accompanied by minor amounts of 1,2-diarylethanes and benzyl chlorides. A mechanism seems likely involving the formation of a benzyltrialkylstannane cation radical, which undergoes C–Sn bond cleavage to afford a benzyl radical. The formation of 1,2-diarylethane from this radical is straightforward, whereas it is suggested that benzyl alcohol and benzaldehyde result from the disproportionation of a benzyloxy radical, formed in a oxygen transfer reaction from iodosylbenzene to the benzyl radical. In CH_2Cl_2, benzyl alcohol can also be the result of hydrogen atom abstraction from the solvent by the benzyloxy radical.

Recently, in our laboratory we have investigated the oxidation of benzyltrimethylsilanes by iodosylbenzene, catalyzed by iron tetrakis(pentafluorophenyl)porphyrin chloride (TPFP)FeCl, a model compound of cytochrome P-450 family of enzymes.[1,2] Through a kinetic and products study, a hydrogen atom transfer mechanism (HAT) has been suggested when the reactions have been carried out in CH_2Cl_2. An (α-hydroxybenzyl)trimethylsilane is formed, which is immediately converted to benzaldehyde under the reaction conditions. However, evidence for the incursion of an electron transfer (ET) mechanism, leading to a benzylic derivative, has been found in the oxidation of (4-methoxybenzyl)trimethylsilane in a more polar solvent (CH_2Cl_2–MeOH–H_2O).[1]

We have considered it of interest to extend this study to the corresponding reactions of benzyltrialkylstannanes for the following reasons. First, since benzyltrialkylstannanes have an oxidation potential lower than that of the corresponding benzyltrialkylsilanes, the former can also react by an ET mechanism under experimental conditions where benzyltrialkylsilanes cannot. Second, benzyltrialkylstannane cation radicals undergo C–Sn bond cleavage much more easily than benzyltrialkylsilane cation radicals, as in these species the C–Sn bond is significantly weaker than the C–Si bond.[3] Thus, the formation of benzylic derivatives is expected to be highly diagnostic with respect to the formation of these reaction intermediates. Finally, very little is known about the reactivity and the fate of tin derivatives in biomimetic and/or enzymatic oxidations, most of the work concerning substrates which do not react by an ET mechanism and therefore do not undergo any C–Sn bond scission.[4]

Scheme 1



In this paper we report on a product study of the oxidations of benzyltrimethylstannane (**1**), (4-methoxybenzyl)trimethylstannane (**2**), benzyltributylstannane (**3**), and (4-methoxybenzyl)tributylstannane (**4**) by iodosylbenzene, catalyzed by (TPFP)FeCl.

Results

The reactions have been carried out, either in dichloromethane or in benzene, at 25 °C, under rigorous exclusion of oxygen (freeze–pump–thaw method), using a 20:20:1 substrate–iodosylbenzene–iron porphyrin molar ratio. Some experiments have also been carried out in CD_2Cl_2 and in a mixed solvent (80:18:2CH_2Cl_2–MeOH–H_2O), hereafter simply indicated as the mixed solvent. After the usual workup (see Experimental Section), product analyses have been carried out by ^1H NMR, GC–MS, and GLC (comparison with authentic specimens). In the oxidations of **1**–**4** in CH_2Cl_2 and in benzene, benzyl alcohols and benzaldehydes have been the main reaction products, accompanied by smaller amounts of the corresponding benzyl chlorides and bibenzyls (Scheme 1).

When the mixed solvent was used, small amounts of benzyl ethers were also formed. Benzaldehydes are, in large part, genuine reaction products since only a limited oxidation of the corresponding alcohols occurs under the reaction conditions (see Experimental Section).

The fate of tin could not be established in detail, and in this respect the tributylstannanes **3** and **4**, used since

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[†] Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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Table 1. Product Yields in the Oxidation of Benzyltrialkylstannanes by PhIO, Catalyzed by (TPFP)FeCl (PhIO, Substrate 0.1 M, (TPFP)FeCl 0.005 M)

		product yields, %[a]			
substrate	solvent	ArCHO	$ArCH_2OH$	$ArCH_2Cl$	$(ArCH_2)_2$
1	benzene	9	6	1	3
2	benzene	16	13	3	5
1	CH_2Cl_2	13	14	3	3
2	CH_2Cl_2	12	11	8	4
3	CH_2Cl_2	8	10	4	4
4	CH_2Cl_2	9	9	3	4
1[b]	CH_2Cl_2	14	9	2	4
2[b]	CH_2Cl_2	14	11	6	2

[a] With respect to the initial moles of substrate, determined by NMR and by GLC in the presence of an internal standard. The average error is 10%. [b] Deoxygenation was carried out only by flushing with argon.

Table 2. Product Yields in the Oxidation of Benzyltributylstannanes by PhIO, Catalyzed by (TPFP)FeCl in a Mixed Solvent (80:18:2 $CH_2Cl_2-CH_3OH-H_2O$)[a]

	product yields, %[b]			
substrate	ArCHO	$ArCH_2OH$	$ArCH_2Cl$	$ArCH_2OCH_3$
3	8	9	5	0.5
4	16	11	6	5

[a] Conditions: PhIO, substrate 0.1 M, (TPFP)FeCl 0.005 M. [b] With respect to the initial moles of substrate, determined by ^1H NMR and by GLC in the presence of an internal standard. The average error is 10%.

Table 3. Product Yields in the Oxidation of Benzyltrimethylstannane (1) and Benzyltributylstannane (3) by PhIO, Catalyzed by (TPFP)FeCl[a]

		product yields, %[b]			
substrate	solvent	PhCHO	$PhCH_2OH$	$PhCH_2Cl$	$(PhCH_2)_2$
1	CH_2Cl_2	13	14	3	3
1	CD_2Cl_2	17	8	2	4
3	CH_2Cl_2	8	10	4	4
3	CD_2Cl_2	12	5	2	4

[a] Conditions: PhIO, substrate 0.1 M, (TPFP)FeCl 0.005 M. [b] With respect to the initial moles of substrate, determined by ^1H NMR and by GLC in the presence of an internal standard. The average error is 10%.

they should lead to heavier tin-containing products, were of no help. However, in CD_2Cl_2, with **1** and **2** as the substrates, a large singlet at *ca.* δ 0.4 in the ^1H NMR spectrum of the final reaction mixture was observed, which may be attributed to a species containing the Sn–O bond, presumably Me_3SnOH or a species derived therefrom (see Experimental Section).

The conversion in products was 20–30%, with a material balance larger than 90%. Appropriate experiments have shown that no products are observed when either (TPFP)FeCl or iodosylbenzene is reacted alone with the benzyltrialkylstannanes.

All results are displayed in Tables 1–3.

Discussion

First of all, it has to be noted that in these reactions only destannylation products are observed. No evidence has been found for the formation of hydroxylated benzylstannanes, either in the side chain or in the ring. Nor does it seem possible (see below) that, as previously observed with benzylsilanes,[1,2] (α-hydroxybenzyl)trialkylstannanes are first formed and then rapidly converted into benzaldehydes under the reaction conditions. Clearly, the cleavage of the C–Sn bond appears to be the key step in the oxidations of benzyltrialkylstannanes catalyzed by (TPFP)FeCl, and it is highly likely that this cleavage occurs in a benzyltrialkylstannane cation radical, since it is well-known that stannane cation radicals undergo very facile scission of the alkyl–metal bond.[5]

The formation of a radical cation intermediate is also suggested by the presence of bibenzyls as well as of benzyl chlorides and benzyl alcohols in the reaction products, which indicates that benzyl radicals are formed in these processes. Thus, the most plausible hypothesis is that the transfer of an electron occurs from the substrate to the iron porphyrin oxo complex, indicated from now on as $P^{\bullet+}-Fe^{IV}{=}O$, suggested to be the active species in iron porphyrin catalyzed oxidations by iodosylbenzene or other oxygen donors.[6] A cation radical forms, which then undergoes C–Sn bond cleavage, presumably assisted by $P-Fe^{IV}{=}O$, giving a benzyl radical (eqs 1 and 2). Cleavage of the Fe–O bond in $P-Fe^{IV}-OSnR_3$ might then occur (eq 3), regenerating $P-Fe^{III}$ and forming a (trialkylstannyl)oxy radical,[7] from which trialkyltin hydroxide and/or other species containing the Sn–O bond may be derived.

$$P^{\bullet+}-Fe^{IV}{=}O + ArCH_2SnR_3 \overset{ET}{\rightleftharpoons} P-Fe^{IV}{=}O + ArCH_2SnR_3^{\bullet+} \quad (1)$$

$$P-Fe^{IV}{=}O + ArCH_2SnR_3^{\bullet+} \rightarrow ArCH_2^{\bullet} + P-Fe^{IV}-OSnR_3 \quad (2)$$

$$P-Fe^{IV}-OSnR_3 \rightarrow P-Fe^{III} + R_3SnO^{\bullet} \quad (3)$$

It is important to note that the electron transfer in eq 1 is certainly feasible from the energetic point of view, since the oxidation potential of $P^{\bullet+}-Fe^{IV}{=}O$ should be higher than 1.6 V *vs* NHE,[8] whereas for the benzyltrialkylstannanes we have estimated an oxidation potential of 1.38 V *vs* NHE for **2** and **4** and of 1.68 V *vs* NHE for **1** and **3** (but still lower values are possible, as discussed in the Experimental Section). Furthermore, the observation that in the reaction of cyclohexyltriphenylstannane with metalloporphyrins and iodosylbenzene no C–Sn bond cleavage products have been observed but only hydroxylated products of the cyclohexane ring[4d] is in line with the previous suggestions. Almost certainly, this finding has to be ascribed to the much higher oxidation potential of cyclohexyltriphenylstannane with respect to benzyltrialkylstannanes, where strong hyperconjugation

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(6) (a) Meunier, B. *Chemical Rev.* **1992**, *92*, 1411. (b) Shelton, R. A., Ed.: *Metalloporphyrins in Catalytic Oxidations;* Dekker: New York, 1994.

(7) Korth, H. G.; Sustmann, R.; Dupuius, J.; Giese, B. *Chem. Ber.* **1987**, *120*, 1197. Even if the reaction shown in eq 3 is not favored on thermodynamics grounds, it might be driven to the right from the subsequent reactions of $R_3SnO^{\bullet}$ (*i.e.* hydrogen atom abstraction, disproportionation).

(8) Sugimoto, H.; Tung, H. C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 2465. In this paper a value of 1.58 V *vs* NHE is reported for the oxidation potential of the oxo complex of iron tetrakis(2,6-dichlorophenyl)porphyrin. Due to the very strong electron attracting power of fluorine atoms a significantly higher $E°$ value is expected for the oxo complex of (TPFP)FeCl.

between the C—Sn bond and the π-system of the aromatic ring is possible.[9]

The benzyl radical might also result from a direct attack on tin by the iron oxo complex (S_H2 reaction).[10] At present, this possibility cannot be excluded with certainty, even if we feel that it is much less likely than that of the operation of an electron transfer mechanism. Accordingly, we have found that the *t*-BuO$^\bullet$ radical (which has been suggested to behave similarly to $P^{\bullet+}—Fe^{IV}=O$ in radical reactions)[11] reacts with benzyltrimethylstannane to give products formed by a predominant hydrogen atom transfer mechanism (see Experimental Section). More significantly, no benzylic derivative attrbutable to the operation of an S_H2 mechanism has been observed.[12] The finding that *t*-BuO$^\bullet$ does not react by an S_H2 mechanism is very important since, apart from the suggested similarity between $P^{\bullet+}—Fe^{IV}=O$ and *t*-BuO$^\bullet$, we should also consider that only a minor part of the spin density is on the oxygen atom of the iron oxo complex.[13] Thus, the tendency to be involved in S_H2 reactions should certainly be higher for *t*-BuO$^\bullet$ than for $P^{\bullet+}—Fe^{IV}=O$.

Coupling of the benzyl radicals leads to bibenzyls (eq 4), whereas benzyl chlorides can be formed either by ligand transfer from the porphyrin and/or by chlorine atom abstraction from the solvent CH_2Cl_2 (eqs 5 and 6).

$$2ArCH_2^\bullet \rightarrow ArCH_2CH_2Ar \qquad (4)$$

$$ArCH_2^\bullet + P—Fe^{III}—Cl \rightarrow ArCH_2Cl + P—Fe^{II} \qquad (5)$$

$$ArCH_2^\bullet + CH_2Cl_2 \rightarrow ArCH_2Cl + {}^\bullet CH_2Cl \qquad (6)$$

It is more difficult to rationalize the formation of the major reaction products benzaldehydes and benzyl alcohols in CH_2Cl_2 or benzene, since the simple possibility that these products arise from the oxidation of the benzyl radical by adventitious oxygen present in the medium can be excluded. As was said before, the reaction mixtures were accurately deoxygenated; moreover, when the deoxygenation procedure used was less accurate (see Table 1, footnote *b*), the amount of aldehyde and alcohol formed did not increase significantly.

Also unlikely is that benzaldehyde is formed by the route shown in eq 7 (formation, by a HAT mechanism, of a hydroxy-substituted benzylstannane which is converted into the aldehyde under the reaction conditions), whereas benzyl alcohol results from the oxidation of the benzyl radical to a benzyl carbocation, which then might react with adventitious water present in the medium (eq 8).

$$ArCH_2SnR_3 \xrightarrow{\text{(TPFP)FeCl, PhIO}} ArCH(OH)SnR_3 \xrightarrow{\text{ox}} ArCHO \qquad (7)$$

$$ArCH_2^\bullet \xrightarrow{\text{ox}} ArCH_2^+ \xrightarrow{H_2O} ArCH_2OH \qquad (8)$$

Accordingly, since the formation of the alcohol would require an ET step and that of aldehyde a HAT step, we would expect that the benzyl alcohol/benzaldehyde molar ratio in the products increases significantly as we decrease the oxidation potential of the substrate, that is, as we move from **1** and **3** to **2** and **4**, respectively. Clearly, the results reported in Table 1 do not support this hypothesis.

Moreover, when the reaction has been carried out in the mixed solvent, we have found that benzyl alcohol is formed in much larger amount than benzyl methyl ether (Table 2), whereas the reverse should be observed if the benzyl cation reacts with the solvent, since MeOH is much more reactive than H_2O toward carbocations[14] and, moreover, in the mixed solvent the MeOH—H_2O molar ratio is 9:1. Interestingly, however, it can be noted that, with **4** as the substrate, which forms the more easily oxidizable 4-methoxybenzyl radical, the relative amount of ether increases, suggesting that, in that case, the pathway indicated in eq 8 might be followed, although as a minor reaction route.

Recently, the intermediacy of cumyloxy radicals has been proposed in the oxidation of cumene by iodosylbenzene, catalyzed by iron and manganese porphyrins and evidence has been obtained that these oxy radicals can be formed by reaction of cumyl radicals with iodosylbenzene as well as with other oxygen donors.[15] On the basis of these results, a reasonable hypothesis that might rationalize the observations reported in this paper is the formation of a benzyloxy radical, by reaction of the benzyl radical with iodosylbenzene (eq 9),[16] which then undergoes a disproportionation reaction,[17] leading to benzyl alcohols and benzaldehydes (eq 10). In addition, in CH_2Cl_2, benzyl alcohols can also result from a HAT reaction of the benzyloxy radical with the solvent (eq 11).

$$ArCH_2^\bullet + PhIO \rightarrow ArCH_2O^\bullet + PhI \qquad (9)$$

$$2ArCH_2O^\bullet \rightarrow ArCHO + ArCH_2OH \qquad (10)$$

$$ArCH_2O^\bullet + SH \rightarrow ArCH_2OH + S^\bullet \qquad (11)$$

This mechanistic hypothesis requires that the alcohol/aldehyde molar ratio should be greater than 1 in dichloromethane and 1 in benzene, and it is rewarding to note that data in Table 1 are quite in agreement with this prediction, especially when it is considered, as pointed out previously, that some alcohol—aldehyde conversion is possible, which should increase the proportion of the aldehyde in the reaction product.

Substantial support for this hypothesis comes also from the finding that when the benzyl radical has been generated, from toluene and *t*-BuO$^\bullet$ in the presence of iodosylbenzene, both benzyl alcohol and benzaldehyde are formed (see Experimental Section). Actually, the amount of aldehyde was in this case, significantly larger than that of the alcohol, but this is most likely due to partial oxidation of the latter compound under the reaction conditions.

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(9) Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 7476.

(10) Davis, A. G.; Roberts, B. P. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; pp 555–557, 572–575.

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(12) This finding should also allow us to exclude the possibility of a reaction of $R_3SnO^\bullet$ with the substrate to give $(R_3Sn)_2O$ and benzyl radicals.

(13) Jørgensen, K. A. In ref 6b, p 77.

(14) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.

(15) Baciocchi, E.; d'Acunzo, F.; Galli, C.; Ioele, M. *J. Chem. Soc., Chem. Commun.* **1995**, 429.

(16) At present, we should also consider the possibility that oxygen is also transferred from $P^{\bullet+}—Fe^{IV}=O$.

(17) Ho, S. K.; de Susa, J. B. *J. Chem. Soc.* **1961**, 1788.

Finally, consistent with the suggested mechanism is the observation (Table 3) that the proportion of benzyl alcohol in the product is significantly decreased when the reaction is carried out in deuterated dichloromethane. Accordingly, in CD_2Cl_2, path 11, which leads only to the alcohol, is depressed by the deuterium kinetic isotope effect. Moreover, the intermediacy of benzyloxy radicals nicely justifies the previously mentioned finding that much more benzyl alcohol than benzyl methyl ether is formed when the reaction is carried out in the mixed solvent, since the benzyloxy radical is expected to abstract a hydrogen atom from either CH_2Cl_2 or methanol to form benzyl alcohol.

The possibility that alkoxy radicals play an active role in iron porphyrin catalyzed oxidations is certainly of great interest for its novelty and the mechanistic implications. Probably, this route becomes very important in the oxidation of benzyltrialkylstannanes because in this reaction the iron oxo complex does not abstract a hydrogen atom from the substrate to form Fe^{IV}—OH and a benzyl radical. Thus, the in-cage oxygen rebound pathway, observed in the corresponding reaction of methylbenzenes and alkanes,[6a] is not possible. Therefore, *all* benzyl radicals have the possibility of escaping from the cage and undergoing other reactions, among which that with iodosylbenzene may play a significant role. It is also very likely that the mechanism suggested here applies as well to the oxidation of (4-methoxybenzyl)trimethylsilane induced by (TPFP)FeCl in the mixed solvent.[18]

Further study to find more information on this mechanistic possibility and to determine its scope is certainly necessary, and work in this respect is under way in our laboratory.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WP80 SY spectrometer and with a Bruker AC 300 P spectrometer. GLC analyses were performed on a Varian Vista 6000 gas chromatograph coupled with a Hewlett-Packard Model 3390 A reporting integrator. Nitrogen was used as carrier gas with FID detection. The GC column used for analyses was a 25 m, 0.32 mm i.d. fused silica CPSil 0V1701 capillary column. GC–MS analyses were performed on a HP 5890 GC equipped with a 15 m, 0.2 mm i.d. silica capillary column coated with methyl silicone gum and coupled with a HP 5970 MSD.

Materials. High-purity commercial solvents (Carlo Erba) were dried with the following procedures: methylene chloride was distilled from P_2O_5 before use; benzene was distilled and kept over sodium wires. Deuterated solvents were purchased from Janssen and kept over anhydrous sodium sulfate. [5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato]iron(III) chloride (TPFP)FeCl was purchased from Aldrich. Iodosylbenzene was prepared by hydrolysis of the corresponding diacetate (Aldrich) with aqueous sodium hydroxide.[19]

Benzyltrimethylstannanes and benzyltributylstannanes were prepared by Grignard reaction of the appropriate benzylmagnesium chloride with trimethyltin chloride or tributyltin chloride (Aldrich) in anhydrous THF as described in the literature[20] and were purified by chromatography on a silica gel column (eluent petroleum ether 30–50 °C/diethyl ether). Benzaldehyde, 4-methoxybenzaldehyde, benzyl alcohol, and 4-methoxybenzyl alcohol were commercially available.

Trimethyltin hydroxide was prepared by hydrolysis of trimethyltin chloride in alkaline water: mp 118–120 °C, lit.[21] mp 118–119 °C; ^{1}H NMR ($CDCl_3$) δ 0.4.

Di-*tert*-butyl peroxalate was prepared (Caution! explosive) by reaction of *tert*-butyl peroxide with oxalyl chloride[22] in C_6D_6 and was stored at −35 °C, under an argon atmosphere.

Oxidation Procedure. All reactions were run under an argon atmosphere in a 5 mL Shlenk flask at room temperature. A suspension of iodosylbenzene (0.1 M), substrate (0.1 M), and catalyst (0.005 M) in the reaction solvent (1–3 mL) was deoxygenated by three freeze–pump–thaw cycles. After 3 h an internal standard was added; then the mixture was reacted with aqueous $Na_2S_2O_5$ in order to reduce the unreacted iodosylbenzene to iodobenzene. The organic phase was dried over anhydrous Na_2SO_4 and analyzed by GLC, GC–MS, and ^{1}H NMR.

The identity of the products was verified by comparison of the spectral properties with authentic specimens and by GC–MS. No product formation was observed in the absence of either iodosylbenzene or the catalyst.

Oxidation of Benzyl Alcohols by Iodosylbenzene. We have checked that, under the reaction conditions, benzyl alcohol and 4-methoxybenzyl alcohol are converted into the corresponding benzaldehydes only to a limited extent. Accordingly, a suspension of benzyl alcohol (0.05 M), iodosylbenzene (0.1 M), and (TPFP)FeCl (0.005 M) in benzene or dichloromethane was stirred for 3 h at room temperature. After workup (see oxidation procedure) the ^{1}H NMR analysis showed that only 8–10% of the benzyl alcohol and 20–25% of the 4-methoxybenzyl alcohol were converted into the corresponding benzaldehydes.

Reaction of Benzyltrimethylstannane with *t*-BuO•. A solution of benzyltrimethylstannane (0.5 mmol) and di-*tert*-butyl peroxalate (*ca.* 0.06 mmol) in 0.8 mL of C_6D_6 was deoxygenated by bubbling with argon for 5 min and then heated at 50 °C for 3 h. The internal standard was added; then the mixture was reacted with aqueous $Na_2S_2O_5$ in order to reduce the unreacted peroxalate. The organic phase was dried over anhydrous Na_2SO_4 and analyzed by ^{1}H NMR and GC–MS. The products were (α-*tert*-butoxybenzyl)trimethylstannane (0.002 mmol), 1,2-diphenyl-1,2-bis(trimethylstannyl)ethane (0.01 mmol), and benzaldehyde (0.006 mmol), probably derived from partial hydrolysis of the *tert*-butoxy derivative, during the workup procedure.

Reaction of Benzyl Radicals with Iodosylbenzene. Benzyl radicals were generated by the reaction of toluene and *t*-BuO•, formed in the thermal decomposition of di-*tert*-butylperoxalate. Thus, when a suspension of toluene (0.94 mmol) and di-*tert*-butylperoxalate (*ca.* 0.03 mmol) in C_6D_6 (1.2 mL) was first bubbled with argon for 5 min and then heated at 50 °C (3 h), only bibenzyl (0.013 mmol) was obtained as the reaction product. However, when the same reaction was carried out in the presence of iodosylbenzene (0.1 mmol), in addition to bibenzyl (0.006 mmol) also benzyl alcohol (0.0006 mmol) and benzaldehyde (0.0016 mmol) were observed.

Estimation of the Oxidation Potentials of Benzyltributylstannanes. Benzyltributylstannane and (4-methoxybenzyl)tributylstannane oxidation potentials were estimated by measuring the $h\nu_{CT}$ values of the charge transfer complexes of these substrates with tetracyanoethylene (TCNE) in CH_2Cl_2 and fitting these values to the $E°/h\nu_{CT}$ correlation existing for a series of methylbenzenes.[23] The equation which describes such correlation is $E°$ (V *vs* NHE) = $0.862h\nu_{CT}$ (eV) − 0.012. The spectra of the charge transfer complexes of TCNE with benzyltributylstannanes in CH_2Cl_2 were recorded on a HP Vectra spectrophotometer at 25 °C, as previously described.[24] Benzyltributylstannane: λ_{max} = 590 nm; $h\nu_{CT}$ =

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(18) Indeed, also in the oxidation of (4-methoxybenzyl)trimethylsilane, catalyzed by (TPFP)FeCl in the mixed solvent,[1] a greater proportion of benzyl alcohol than benzyl methyl ether has been observed.

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2.1 eV; $E^\circ = 1.68$ V. (4-methoxybenzyl)tributylstannane: $\lambda_{max} = 708$ nm; $h\nu_{CT} = 1.75$ eV; $E^\circ = 1.38$ V. Reasonably, almost identical values are assumed for **1** and **3**, respectively.

It should be noted, however, that the actual values might be lower than those estimated by the above procedure if, as recently suggested,[25] the reorganization energies associated with electron transfer of alkylstannanes are larger than those of alkylbenzenes.

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