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Borane-induced radical reduction of 1-alkenyl- and 1-alkynyl-λ^3-iodanes with tetrahydrofuran

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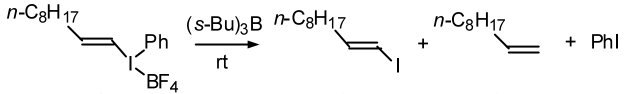
Abstract—Exposure of 1-alkenyl(phenyl)- and 1-alkynyl(phenyl)-λ^3-iodanes to THF at room temperature in the presence of a catalytic amount of trialkylborane results in smooth reduction to give 1-iodo-1-alkenes and 1-iodo-1-alkynes as major products, respectively. The key step in the reductions probably involves a single-electron transfer from α-tetrahydrofuryl radical to the λ^3-iodanes, which generates the labile [9-I-2] iodanyl radicals.

Unsaturated phenyl-λ^3-iodanes (phenyliodonium salts) with 1-alkenyl or 1-alkynyl group as a carbon ligand on the iodine(III) are versatile agents in organic synthesis.[1] Because of the powerful electron-withdrawing nature[2] and the excellent nucleofugality of the phenyl-λ^3-iodanyl groups, which show a leaving group ability about 10^6 times greater than triflate,[3] these λ^3-iodanes serve as highly activated species of the corresponding halides in nucleophilic substitution reactions and as excellent progenitors for generation of alkylidene carbenes.[1]

Little is known, however, for the reduction of these unsaturated 1-alkenyl- and 1-alkynyl-λ^3-iodanes. Chromium(II)-mediated reductive coupling of these unsaturated λ^3-iodanes with aldehydes involves a single-electron transfer from anhydrous chromium dichloride to the λ^3-iodanes generating 1-alkenyl- and 1-alkynylchromium(III) species.[4,5] Diaryl-λ^3-iodanes with a weakly nucleophilic heteroatom ligands (e.g. BF_4, PF_6, and SbF_6) are efficient photoinitiators for cationic polymerization of three- to five-membered cyclic ethers and vinyl ethers.[6] The photocurable cationic polymerization finds many commercial applications in areas such as photo imaging, coating, adhesives, inks, and photoresists.[7] The key step in this photoinitiated polymerization involves a single-electron reduction of diaryl-λ^3-iodanes by ether-derived radicals.[8] We report herein trialkylborane-induced reduction of 1-alkenyl- and 1-alkynyl(phenyl)-λ^3-iodanes with THF, which probably proceeds via a single-electron transfer from α-tetrahydrofuryl (α-THF) radical to the λ^3-iodanes (Scheme 1).

Exposure of (*E*)-1-decenyl(phenyl)-λ^3-iodane **1a** to tri(*sec*-butyl)borane (1.3 equiv.) in THF at room temperature for 1 h under argon resulted in smooth reductive fragmentation of the λ^3-iodane and afforded (*E*)-1-iodo-1-decene (**2a**) as a major product in an 82% yield, along with formation of a small amount of 1-decene (**3a**) (14%) and iodobenzene (17%). Comparable results were obtained in the reaction under atmospheric conditions (Table 1, entry 2). Nature of the solvents used in the reaction exerts a significant effect upon the reductive fragmentation of the λ^3-iodane **1a**: thus the reduction of **1a** also takes place smoothly in methanol, *iso*-propanol, and 1,3-dioxolane, but not in benzene and DMF. The former solvents including THF are known to be good hydrogen atom donors. Although no appreciable effects of molecular dioxygen were observed in the reduction of **1a** (Table 1, entry 2), the radical nature of the reductive fragmentation was substantiated by inhibition of the reaction with the added radical scavenger 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) (Table 1, entry 3); in this reaction, a large amount of **1a** was recovered unchanged. Use of a catalytic amount of tri(*sec*-butyl)borane gave a 75% yield of (*E*)-1-iodo-1-decene (**2a**) (Table 1, entries 9 and



1a **2a** **3a**

Scheme 1.

Keywords: reduction; λ^3-iodane; radical; borane.

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Table 1. Reduction of (*E*)-1-decenyl(phenyl)-λ^3-iodane **1a**[a]

Entry	*s*-Bu_3B (equiv.)	Solvent	*t* (h)	Product (% yield[b])			Ratio **2a**:PhI
				2a	**3a**	PhI	
1	1.3	THF	1	82	14	17	83:17
2	1.3	THF	1[c]	83	16	17	83:17
3	1.3	THF	1[d]	–	1	11[e]	–
4	1.3	MeOH	5	68	9	28[f]	71:29
5	1.3	*i*-PrOH	1	54	23	26[g]	68:32
6	1.3	1,3-Dioxolane	1	54	23	41	57:43
7	1.3	PhH	1	5	1	6	45:55
8	1.3	DMF	1	–	–	10	–
9	0.3	THF	3	75	14	25	75:25
10	0.1	THF	3	75	14	25	75:25
11	0.1[h]	THF	3	72	14	23	76:24
12	0.1[i]	THF	3	54	9	27	67:33

[a] Unless otherwise noted, reduction of **1a** [0.02 M] was carried out in the presence of *s*-Bu_3B at room temperature under argon.
[b] GC yields.
[c] Under atmospheric conditions.
[d] The reaction was carried out in the presence of TEMPO (1.3 equiv.).
[e] λ^3-Iodane **1a** (69%) was recovered unchanged.
[f] ^1H NMR yields.
[g] Formation of acetone (89%) was detected by GC.
[h] Et_3B was used.
[i] *n*-Bu_3B was used.

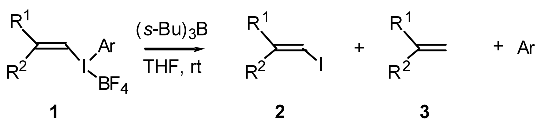
10).[9] Both triethylborane and tributylborane are found to be effective catalysts in the reduction.

(*Z*)-β-Acetoxyvinyl(phenyl)-λ^3-iodanes **1c** and **1d** undergo the reductive fragmentation under our conditions using a catalytic amount (0.3 equiv.) of tri(*sec*-butyl)borane and afforded (*Z*)-2-acetoxy-1-iodo-1-alkenes **2** stereoselectively in high yields (Table 2, entries 2 and 3). Decreased yield of (*Z*)-2-chloro-1-iodo-1-alkene **2** was obtained by the reduction of (*Z*)-β-chlorovinyl-λ^3-iodane **1e**. Entries 5 and 6 in Table 2 illustrate some substituent effects upon the regioselectivity for the aryl–iodine(III) to the vinyl–iodine(III) bond cleavage in the borane-catalyzed reductive fragmentation: the ratios of products, vinyl iodide **2** to aryl iodide, changed from 75:25 in **1a** (Table 1, entry 9) to 64:36 by the introduction of an electron-donating *p*-Me group in **1f**, while to 87:13 in the reduction of 1-decenyl (*para*-chlorophenyl)-λ^3-iodane **1g**.

Trialkylborane-catalyzed reduction of 1-alkynyl-(phenyl)-λ^3-iodanes **4** in THF at room temperature affords 1-iodoalkynes **5** in high yields (Table 3). In the reduction, higher selectivity of more than 90% for the aryl–iodine(III) over the alkynyl–iodine(III) bond cleavage was observed, compared to that of (*E*)-1-decenyl-λ^3-iodane **1a**.

As illustrated in Scheme 2, a mechanism for the reduction of (*E*)-1-decenyl-λ^3-iodane **1a** might be assumed to involve the following key steps: (a) α hydrogen atom abstraction of THF with *sec*-butoxy and/or *sec*-butyl radicals generated by the reaction of tri(*sec*-butyl)borane with O_2,[10] producing α-tetrahydrofuryl radical **7** as an initiation step, (b) a single-electron transfer from α-THF radical **7** to the λ^3-iodane **1a**, which generates labile [9-I-2] iodanyl radical **8** and oxonium ion **9**,[11] (c) self- decomposition of the iodanyl radical **8** to a combination of (*E*)-1-iodo-1-decene (**2a**) and phenyl radical, which in turn abstracts an α hydrogen atom of THF with liberation of benzene.[12] Thus, the α-THF radical **7** is regenerated and constitutes a

Table 2. Reduction of 1-alkenyl(aryl)-λ^3-iodanes **1**[a]

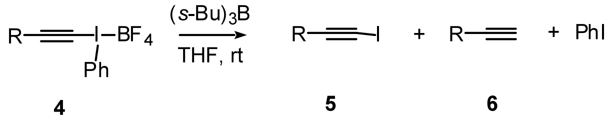


b: R^1 = $Ph(CH_2)_3$, R^2 = H, Ar = Ph; **c**: R^1 = *n*-C_8H_{17}, R^2 = OAc, Ar = Ph;
d: R^1 = $Ph(CH_2)_3$, R^2 = OAc, Ar = Ph; **e**: R^1 = *n*-C_8H_{17}, R^2 = Cl, Ar = Ph;
f: R^1 = *n*-C_8H_{17}, R^2 = H, Ar = *p*-MeC_6H_4;
g: R^1 = *n*-C_8H_{17}, R^2 = H, Ar = *p*-ClC_6H_4

Entry	**1**	*t* (h)	Product (% yield[b])			Ratio
			2	**3**	ArI	**2**:ArI
1	**1b**	5	89[c]	–	–	–
2	**1c**	1	81[c]	13	–	–
3	**1d**	1	85[c]	5	–	–
4	**1e**[d]	2	48	17	34	59:41
5	**1f**	3	60	31	34[e]	64:36
6	**1g**	2	87	8	13[f]	87:13

[a] Unless otherwise noted, the reaction was carried out in the presence of *s*-Bu_3B (0.3 equiv.) in THF at room temperature under argon.
[b] GC yields.
[c] Isolated yields.
[d] *s*-Bu_3B (1 equiv.) was used.
[e] Toluene was obtained in 66% yield (GC).
[f] Chlorobenzene was obtained in 83% yield (GC).

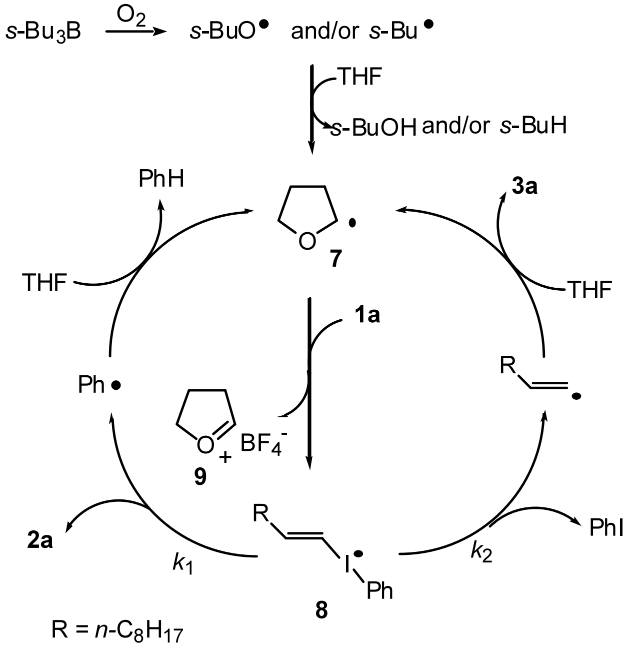
Table 3. Reduction of 1-alkynyl(phenyl)-λ^3-iodanes **4**[a]



a: R = n-C_8H_{17}; **b**: R = $Me_2CH(CH_2)_2$; **c**: R = $Ph(CH_2)_3$

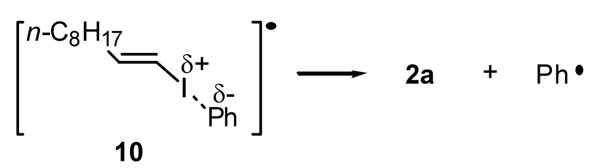
Entry	4	t (h)	Product (% yield[b])			Ratio
			5	**6**	PhI	**5**:PhI
1	**4a**	3	91	9	5	94:6
2	**4b**	3	94	1	8	92:8
3	**4c**	3.5	97	3	3	97:3

[a] Unless otherwise noted, the reaction was carried out in the presence of s-Bu_3B (0.1 equiv.) in THF at room temperature under argon.
[b] GC yields.

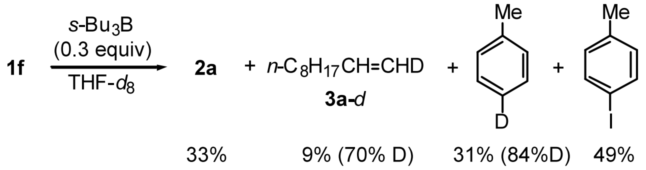


Scheme 2.

catalytic cycle. As a minor process, cleavage of the vinylic carbon–iodine bond in **8** produces a terminal vinyl radical with the formation of iodobenzene. The vinyl radical also abstracts hydrogen of THF to give the α-THF radical **7**, which creates the other catalytic cycle.



Scheme 3.

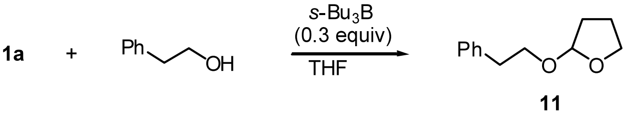


Scheme 4.

Diphenyliodanyl radical $Ph_2I^•$ decays very quickly to iodobenzene and phenyl radical with the life time of 0.2 ns,[13,14] and therefore the analogous [9-I-2] iodanyl radical **8** should be highly labile. Self-decomposition of the iodanyl radical **8** constitutes a product determining step (k_1 versus k_2). It has been well established that the decomposition of aryl(phenyl)iodanyl radicals $ArPhI^•$ favors cleavage of the Ar–I bond if the aryl groups have electron-withdrawing substituents, whereas cleavage of the Ph–I bond is preferred when the aryl groups bear electron-donating substituents.[4a] Our results, shown in entry 9 in Table 1, and entries 5 and 6 in Table 2, are in line with this observation.[15] A Hammett plot of log (k_1/k_2) versus σ is linear with $\rho = 1.4$ and correlation coefficient = 1.00. For the self-decomposition of **8**, a polar transition state **10**, shown in Scheme 3, with partial charge separation is in a good agreement both with the observed cleavage aptitudes and with the positive ρ value of the Hammett plots.[4a,16]

In the reduction of 1-alkynyl(phenyl)-λ^3-iodanes **4**, the observed high selectivity for the phenyl–iodine(III) bond cleavage yielding 1-iodoalkynes **5** (Table 3) is not compatible with the polar transition state yielding 1-alkynyl radicals, in which partial negative charge is mostly developed on the *sp* carbon atoms. Selective formation of 1-alkynyl radicals during decomposition of the [9-I-2] 1-alkynyl(phenyl)iodanyl radicals seems to be very difficult, because of the highly energetic nature of the radicals: the stabilization energy (SE° = −15.57 kcal/mol) of $HC{\equiv}C^•$ is smaller than that of the phenyl radical (−10.27 kcal/mol).[17] Photochemical decomposition of (3,3-dimethyl-1-butynyl)(phenyl)-λ^3-iodane in ethanol[18] and reduction of **4a** with tetrakis(dimethylamino)ethylene,[4a] both of which generate the corresponding [9-I-2] iodanyl radicals, are shown to undergo cleavage of the phenyl–iodine(III) bond with high selectivity. These results suggest the intervention of 1-alkynyl(phenyl)iodanyl radicals in the reduction of **4** by THF under our conditions.

Evidence for generation of both aryl and alkenyl radicals through facile decomposition of [9-I-2] 1-alkenyl(aryl)iodanyl radicals, followed by abstraction of an α hydrogen atom of THF, was obtained by the reaction of (E)-1-decenyl(p-tolyl)-λ^3-iodane **1f** in THF-d_8 at room temperature (5 h/Ar). GC–MS analysis showed 70 and 84% deuterium incorporations in 1-decene **3a** and toluene, respectively (Scheme 4). In the reduction of λ^3-iodane **1a** in methanol and *iso*-propanol (Table 1, entries 4 and 5), these alcohols act as good hydrogen atom donors toward phenyl and vinyl radicals to generate α-hydroxy carbon-centered radicals, which in turn serve as efficient reductants for **1a**. In fact, it has been shown that 2-hydroxy-2-propyl radical undergoes a facile single-electron transfer to diphenyl-λ^3-iodanes to



Scheme 5.

generate [9-I-2] diphenyliodanyl radical.[19] Formation of a large amount of acetone (Table 1, entry 5) is compatible with this mechanism.

Mechanism for borane-induced reduction of λ^3-iodane **1a** in THF, shown in Scheme 2, involves generation of THF-derived oxonium ion **9**. Formation of the oxonium ion **9** in the reaction was firmly established by the detection of oxonium ion-derived acetals: for instance, when the reduction of **1a** was carried out in the presence of 1 equiv. of 2-phenylethanol as a trapping agent of the oxonium ion **9** (room temperature/1 h/Ar), THF adduct **11** was produced in 59% yield, along with the formation of **2a** (81%) and **3a** (14%) (Scheme 5). Similarly, the acetal **11** was obtained in 51% yield in the reaction of 1-decynyl(phenyl)-λ^3-iodane **4a** under the conditions.

Thus, we have developed a method for radical-chain reduction of 1-alkenyl(phenyl)- and 1-alkynyl(phenyl)-λ^3-iodanes by THF, which involves a single-electron transfer from α-tetrahydrofuryl radical to the λ^3-iodanes.

Acknowledgements

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