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Fast Tin-Free Hydrodehalogenation and Reductive Radical Cyclization Reactions: A New Reduction Process

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The photostimulated reactions of several aryl and alkyl chlorides and bromides with the monoanion of reduced ethyl benzoate **5H** furnish the reduced products in high yields. If the aryl moieties have suitable double bonds, the cyclized reduced products are obtained in high yields. The photostimulated reaction of 1-allyloxy-2-bromobenzene (**1a**) with **5H** affords 3-methyl-2,3-dihydro-benzofuran (**2a**) in 97% yield. When 1-allyloxy-2-chlorobenzene (**1b**) is used, the yield of **2a** is only 55%, which increases up to 91% when acetone enolate ion is added to the reaction mixture as entrainment reagent. With diallyl-(2-bromophenyl)amine (**3a**), and 2-allyloxy-1-halonaphthalenes (chloro, **4b**, and bromo, **4a**) the cyclized reduced products are obtained in yields above 96%. By competition experiments, **5H** reacts ca. 5 times faster with 1-naphthyl radicals than benzenethiolate ions do, which is near the diffusion limit rate.

Introduction

Tin hydrides, mainly tri-*n*-butylstannane (*n*-Bu_3SnH) and trimethylstannane (Me_3SnH), play a central role in radical chemistry.[1] However, their utility at preparative levels is usually limited due to their toxicity and difficulty of elimination from reaction mixtures. Special efforts have been attempted in order to replace the toxic tin hydrides, and potential substitute candidates were reported in the last years.[2] *n*-Bu_3SnH is a very versatile reagent, since the abstraction of hydrogen generates the tin-centered radical $Bu_3Sn^•$, which readily reacts in a selective manner with a wide range of substrates such as selenides, xanthates, sulfides, and alkyl and aryl halides.

Special workup procedures and purification protocols, systems that use tin hydride in catalytic amounts, and fluorous and polymeric tin hydrides have been developed with the aim to replace stannanes, but usually traces of tin remain in the reaction products.[1]

Tris(trimethylsilyl)silane (TTMSS) is one of the best options to replace tin hydrides, and reductive cyclization reactions have been performed with this reagent.[3] Although TTMSS is not toxic and can be easily eliminated from the reaction mixtures, it suffers disadvantages derived from its cost and difficulty of storage. Furthermore, the radical $(TMS)_3Si^•$ can react with double bonds and this may be an inconvenience in reductive radical cyclization reactions. This reagent is slightly less reactive than *n*-Bu_3SnH, and many kinetic parameters are known.[4]

Germanium hydrides, especially *n*-Bu_3GeH and tri-2-furylgermane,[5] can also be employed for this type of reaction but are too expensive to have practical applications. Germanium hydrides are less reactive than tin hydrides but they react faster with double bonds. Studer et al.[6] have recently described the use of new silylated cyclohexadienes as powerful and easily available reagents to perform radical reactions. These compounds are less reactive than TTMSS but more stable, and they can easily be handled and eliminated from the reaction mixtures.

Phosphorus reagents constitute an active field of work since they are nontoxic and inexpensive.[7] Much attention has been centered especially on *N*-ethylpiperidine hypophosphite and phosphinic acid, but since phosphorus-centered radicals are less reactive than those derived from tin and silicon, only halides with weak carbon−halogen bonds can be employed.

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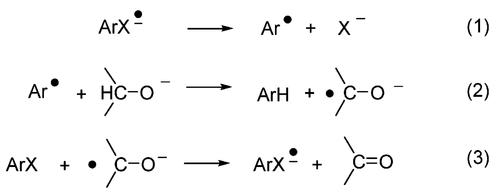
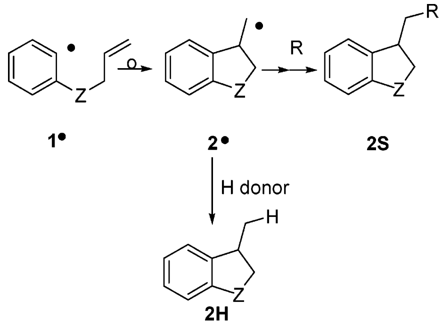
10.1021/jo035477i CCC: $27.50

SCHEME 1



SCHEME 2



A NaBH$_4$/10-methyl-9,10-dihydroacridine system has been used to perform radical cyclizations of suitably substituted aryl halides.[8]

Hydrodehalogenation reactions of aryl halides by use of alkoxide ions with α-hydrogens is a well-established process, and the kinetics and influence of substituent groups have been studied.[9] The steps of this chain reaction are shown in Scheme 1.

After electron transfer to ArX and ensuing fragmentation, an aryl radical is formed (eq 1). The alkoxide ion transfers the α-hydrogen to the radical Ar$^•$ to form the reduced product ArH, and the radical anion of a carbonyl compound is generated (eq 2). This can ultimately propagate the chain reaction (eq 3).

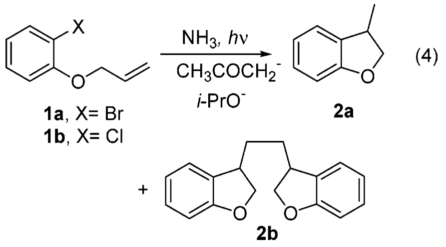
On the other hand, radical ring closure by intramolecular addition of a radical to a double bond is a well-known process.[10] The general reaction pathway is depicted in Scheme 2 and involves the generation of the aromatic radical **1**$^•$, followed by cyclization with a tethered double bond in a 5-exo trig fashion to afford the radical **2**$^•$. This radical can be reduced with a hydrogen donor to obtain a reduced cyclized product (**2H**)[11] or can be further reacted with different reagents to yield substituted cyclized compounds (**2S**).[12]

In this work we report a new nontoxic and readily available reactive intermediate that can be used both for tin-free reductive cyclization of suitably substituted aryl halides and for hydrodehalogenation of aryl and alkyl halides.

Results and Discussion

We have recently described the synthesis of substituted heterocyclic compounds by tandem 5-exo trig ring closure–S$_{RN}$1 reaction with different nucleophiles and adequately substituted aryl halides.[13] To extend the scope of this methodology, we decided to explore the possibility of preparing the cyclized reduced products. The fact that ring closure is a unimolecular process, and therefore does not depend on the concentration of the reduction reagent, led us to the reasonable belief that, under controlled experimental conditions (diluted conditions), the ring closure–reduction process would be obtained in one-pot reactions by a tandem cyclization–reduction sequence.

We studied the photoinduced reductive cyclization of 1-allyloxy-2-bromobenzene (**1a**) with a mixture of acetone enolate ions (to initiate the reaction)[14] and *i*-PrO$^-$ ions as hydrogen source. These ions were formed in liquid ammonia employing 2-propanol and acetone, with *t*-BuOK in excess. Upon irradiation, a mixture of 3-methyl-2,3-dihydrobenzofuran (**2a**) and dimer **2b** was obtained. By GC–MS analysis, an olefinic derivative of **2a** was found in 22% yield, probably arising from disproportionation of the radical intermediate. This olefinic product could not be isolated from the reaction mixture, due to the comparable polarity (in radial thin-layer chromatography) and similar retention times as observed for **2a**. An excess of *i*-PrO$^-$ ions does not lead to an increase in the yield of **2a** (experiments 1 and 2, Table 1) (eq 4).



Under irradiation, **1a** accepts an electron to afford a radical anion, which fragments to yield radical **1**$^•$ (Z = O in Scheme 2), that cyclizes to radical **2**$^•$ faster than the reduction proceeds. Under these reaction conditions, hydrogen transfer from *i*-PrO$^-$ ions is not fast enough to compete effectively with disproportionation or dimerization of radical **2**$^•$ (Z = O in Scheme 2).

When diallyl-(2-bromophenyl)amine (**3a**), or 2-allyloxy-1-bromonaphthalene (**4a**) was employed as substrate, 1-allyl-3-methyl-2,3-dihydro-1*H*-indole (**3c**) (eq 5) or

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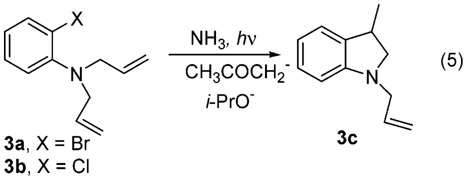
TABLE 1. Photostimulated Hydrodehalogenation and Reductive Cyclization of Organohalides with Different Reagents[a]

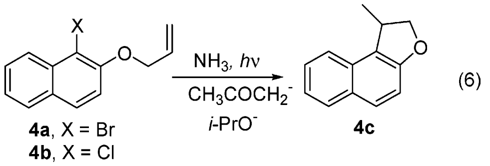
expt	substrate	reagent[b]	X^- [c]	products (% yield)[d]
1	1a	A	90	**2a** (43), **2b** (11)
2	1a	A[e]	95	**2a** (44), **2b** (10)
3	1a	**5H**, i-PrO$^-$	100	**2a** (95), **2c** (4)
4	1a	B	100	**2a** (97), **2c** (3)
5	1a	B[f]	<3	2a (0)
6	1a	B[g]	41	**2a** (38), **2c** (1)
7	1b	B	63	**2a** (55), **2c** (4)
8	1b	B[h]	96	**2a** (91), **2c** (7)
9	3a	A	94	**3c** (60)
10	3a	B	100	**3c** (98)
11	3b	B[h]	68	**3c** (67)
12	4a	A	65	**4c** (50)
13	4a	B	95	**4c** (100)
14	4b	B[h]	93	**4c** (96)
15	6	B	93	**7** (89)
16	1-AdBr	B	81	AdH (70)
17	1-AdCl	B[h]	52	AdH (50)
18[i]	6	**5H**, PhS$^-$	*j*	**7** (78 ± 2), **8** (16 ± 2)
19[i,k]	6	**5H**, PhS$^-$	*j*	**7** (71), **8** (15)
20[k]	8	5H		**8** (100)

[a] All reactions were performed in liquid ammonia and irradiated for 2 h with two water-cooled medium-pressure Hg lamps; the concentration of the substrates was 3.3×10^{-3} M, acetone enolate ion was 3.3×10^{-3} M; i-PrO$^-$ was 6.6×10^{-3} M, and **5H** was 6.6×10^{-3} M, unless otherwise indicated. [b] Reduction reagents: A, $CH_3COCH_2^-$ and i-PrO$^-$ ions; B, **5H** and t-BuO$^-$ ions. [c] Determined potentiometrically. [d] Determined by GC analysis by the internal standard method with authentic samples as references. [e] The concentration of i-PrO$^-$ ions was 9.9×10^{-3} M. [f] Dark conditions, **1a** was recovered in 97%. [g] To the solution was added 20 mol % *p*-dinitrobenzene; **1a** was recovered in 52% yield. [h] With 1.3×10^{-2} M **5H** and $CH_3COCH_2^-$ ions. [i] The concentrations were 0.010 M for **5H** and PhS$^-$ ion and 0.0050 M for **6**. The reaction was performed twice. [j] Not determined. [k] Irradiation time was 15 min.

1-methyl-1,2-dihydro-naphtho[2,1-*b*]furan (**4c**) (eq 6) was obtained in moderate yields (experiments 9 and 12, Table 1).



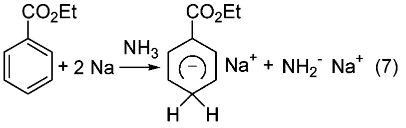
3a, X = Br
3b, X = Cl
3c
(5)



4a, X = Br
4b, X = Cl
4c
(6)

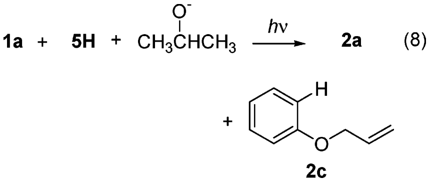
In conclusion, the attempted photoinduced reductive method with acetone enolate/i-PrO$^-$ ions is not effective, and the target products were obtained in poor yields in a mixture difficult to separate.

We found that substitution on aryl iodides by the $S_{RN}1$ mechanism[15] with anions derived from benzoate esters obtained by reaction of the latter with sodium metal in liquid ammonia does not occur, and only reduced products are obtained. When sodium metal is added to a liquid ammonia solution of ethyl benzoate **5**, a deep brown solution of **5H** anion is obtained according to the reaction depicted in eq 7.



5 **5H**
(7)

The NH_2^- ions generated during the formation of **5H** were neutralized with i-PrOH, and a mixture of **5H** and i-PrO$^-$ ions was obtained. When a solution of **5H**, i-PrO$^-$ ions, and **1a** is irradiated (366 nm), a clean and quantitative reaction takes place in which **2a** was formed in high yield together with small amounts of the uncyclized product **2c** (eq 8; experiment 3, Table 1).



(8)
2c

To assess the contribution of **5H** in the reduction of **1a**, the amide ions formed during the generation of reducing reagent **5H** (eq 7) were neutralized with t-BuOH, which generates t-BuO$^-$ ions that do not bear α-hydrogens and therefore lack reducing ability. Now **2a** was obtained in high yields (experiment 4, Table 1), indicating that **5H** not only is a very effective hydrogen donor but also can initiate and propagate the reduction process.

In dark conditions there is no reaction of **1a** with **5H** and t-BuO$^-$, and the photostimulated reaction is inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions (experiments 5 and 6, Table 1).[15] These results indicate that by irradiation **5H** transfers one electron to **1a** to initiate the chain reaction. It is known that the higher the pK_a of the ketones and related compounds, the higher the electron-donor capability of its conjugated base and so the higher the probability of photostimulated electron transfer (ET) reaction.[15,16] The fact that the reaction is inhibited by *p*-DNB indicates the presence of radical anions as intermediates.

Under irradiation, **1a** accepts an electron to give the radical anion **1a**$^{\bullet -}$, which fragments to afford the radical **1**$^\bullet$ (Z = O in Scheme 2) that mainly cyclizes to afford radical **2**$^\bullet$ (Z = O in Scheme 2) with almost no uncyclized reduction product (i.e., **2c**, eq 8) observed (eq 9). Radical **2**$^\bullet$ (Z = O in Scheme 2) reacts fast with **5H** to yield **2a** and the radical anion **5**$^{\bullet -}$, whereupon dimerization or disproportionation reactions do not take place (eq 10). Radical anion **5**$^{\bullet -}$ is able to continue the chain propagation steps (eq 11). The driving force for the fast hydrogen transfer reaction from **5H** to **2**$^\bullet$ (eq 10) is the rearomatization of **5H** to give radical anion **5**$^{\bullet -}$.

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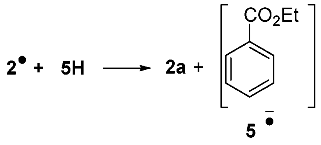
$$\mathbf{1a} \xrightarrow[\text{ET}]{h\nu} \mathbf{1a}^{\bullet -} \rightarrow 1^{\bullet} \rightarrow 2^{\bullet} \qquad (9)$$



(10)

$$\mathbf{5}^{\bullet -} + \mathbf{1a} \rightarrow \mathbf{5} + \mathbf{1a}^{\bullet -} \qquad (11)$$

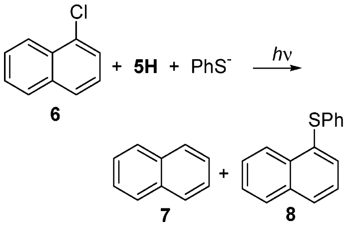
Even aryl chlorides do react with **5H**; i.e., when substrate **1b** is brought into reaction, **2a** is obtained in 55% yield. When the reaction was performed with acetone enolate ion as entrainment reagent to facilitate initiation, high yields of **2a** were obtained (experiments 7 and 8, Table 1).

The photostimulated reactions of substrates **3a**, **4a**, and **4b** with **5H** yield the cyclized reduced products almost quantitatively. In these reactions no uncyclized products were detected (experiments 10, 13, and 14, Table 1).

Other aryl halides react under irradiation with **5H**. Thus, naphthalene (**7**) is formed in 89% yield when 1-chloronaphthalene (**6**) is allowed to react with **5H** (experiment 15, Table 1).

In the photostimulated reaction of 1-bromoadamantane (1-AdBr) with **5H**, adamantane was obtained in good yield. The yield of adamantane was 50% when 1-AdCl was the substrate employed (experiments 16 and 17, Table 1)

The rate constant of the reaction of 1-naphthyl radical with PhS^- ion in liquid ammonia has been determined electrochemically and a value of 2.0×10^{10} M^{-1} s^{-1} has been reported.[17] This prompted us to perform competition experiments between **5H** and PhS^- ion to determine the value of k_H for this very reactive intermediate. When a mixture of **5H**, PhS^- ions, and **6** is irradiated for 2 h, **7** is obtained as the main product together with 1-phenylsulfanylnaphthalene (**8**) (eq 12).



(12)

As product **8** may undergo secondary photolysis to afford **7**, we carried out the irradiation for only 15 min, but similar yields of **7** and **8** were found. When **8** was irradiated under the same experimental conditions, **7** was not formed (experiments 18–20, Table 1). These results show that **5H** is ca. 5-fold more reactive than PhS^- ion toward 1-naphthyl radical, whose coupling reaction has been reported to be near the diffusion limit rate.

In summary, we report the generation and use of a new hydrogen-donor reagent derived from nontoxic, reusable, and inexpensive ethyl benzoate. It can be employed for reductive cyclization of adequately substituted aryl halides and for the hydrodehalogenation of other aryl and alkyl halides. The competition experiments of PhS^- ions with 1-naphthyl radical indicate that the reduction process is very effective and probably near diffusion limit rates.

Experimental Section

Materials. Acetone, *i*-PrOH, and *t*-BuOH were double-distilled and stored over molecular sieves (4 Å). Ethyl benzoate, 1-bromoadamantane, 1-chloroadamantane, 1-chloronaphthalene, adamantane, naphthalene (**7**), allyloxybenzene (**2d**), and benzenethiol were commercially available. All solvents were analytical-grade and were used as received from the supplier. 1-Allyloxy-2-bromobenzene (**1a**),[13] 1-allyloxy-2-chlorobenzene (**1b**),[13] *N*,*N*-diallyl-(2-bromophenyl)amine (**3a**),[13] *N*,*N*-diallyl-(2-chlorophenyl)amine (**3b**),[13] 2-allyloxy-1-bromonaphthalene (**4a**),[13] 2-allyloxy-1-chloronaphthalene (**4b**),[13] and 1-phenylsulfanylnaphthalene (**8**)[18] were prepared as previously reported. Plates (2-mm silica gel 60 PF_{254}) were used for radial thin-layer chromatography purification with hexanes–dichloromethane mixtures as eluants.

Products. 3-Methyl-2,3-dihydrobenzofuran (**2a**),[19] 1,2-bis-(dihydrobenzofuran-3-yl)ethane (**2b**),[20] 1-allyl-3-methyl-2,3-dihydro-1*H*-indole (**3c**),[21] and 1-methyl-1,2-dihydronaphtho-[2,1-*b*]furan (**4c**)[22] were purified by radial thin-layer chromatography with hexanes–dichloromethane mixtures as eluants. Spectral data obtained match well with those previously reported. Adamantane, naphthalene (**7**), allyloxybenzene (**2c**), and 1-phenylsulfanylnaphthalene (**8**) were identified in the reaction mixtures by spike experiments with authentic samples.

Photostimulated Reactions of 1a, 3a, and 4a with Acetone Enolate Anion and *i*-PrO⁻ Ions (Experiments 1, 2, 7, and 10). Into a three-necked round-bottomed flask equipped with a coldfinger condenser charged with ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 300 mL of ammonia previously dried with sodium metal under nitrogen. Acetone (1.0 mmol), *i*-PrOH (2.0 mmol), and *t*-BuOK (3.5 mmol) were added, with 15 min of waiting for acetone enolate and *i*-PrO⁻ ion formation. The substrates (1.0 mmol) were previously dissolved in 1 mL of dried ethyl ether and added to the ammonia solution. The reaction mixtures were irradiated for 120 min with two medium-pressure mercury lamps emitting maximally at 366 nm. The reactions were quenched with ammonium nitrate in excess and then ethyl ether was added. After evaporation of ammonia, the organic phase was extracted with water. The aqueous phase was extracted twice with ethyl ether and reserved for halide titration. The combined organic phases were dried over anhydrous sodium sulfate and evaporated in a vacuum. The products were separated by radial thin-layer chromatography. In experiment 2, 3.0 mmol of *i*-PrOH was used together with 4.5 mmol of *t*-BuOK. For quantitative purposes, an adequate internal standard was added prior to ammonia evaporation.

Photostimulated Reactions with 5H. Into a three-necked round-bottomed flask equipped with a coldfinger condenser charged with ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 300 mL of ammonia previously dried with sodium metal under nitrogen. To the ammonia, ethyl benzoate was added (2.0 mmol) and then sodium metal (4.1 mmol), with 15 min of waiting for **5H** formation. *i*-PrOH (experiment 3) or *t*-BuOH (experiments 4, 5, 8, 11, 13, and 14) (2.0 mmol) was then added. The substrates (1.0 mmol) were dissolved in 1 mL

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of dried ethyl ether and added to the solution and irradiated as indicated in Table 1. The workup was similar to previously indicated. Products **2a**, **3c**, and **4c** were purified as mentioned above. For quantitative purposes, an adequate internal standard was added prior to ammonia evaporation.

In experiments 6, 9, 12, and 15, 4.0 mmol of ethyl benzoate, 8.4 mmol of sodium metal, and 4.0 mmol of acetone were used.

Reaction with 5H in the Dark. The procedure was similar to that for the previous reaction, except that the reaction flask was wrapped with aluminum foil.

Inhibited Photostimulated Reaction with 5H. The procedure was similar to that for the previous reaction, except that *p*-DNB (20 mol %) was added to the solution of nucleophile prior to substrate addition.

Competition Experiment of 5H and Benzenethiolate Ion (Experiments 16 and 17). The generation of **5H** was carried out as indicated previously, except that in this case 200 mL of ammonia was used and the amide ions were neutralized with thiophenol (2.0 mmol) to obtain benzenethiolate ions. 1-Chloronaphthalene was dissolved in 1 mL of dried ethyl ether and added to the ammonia solution of the competing anions. The reaction was irradiated for the time indicated, and after quenching with ammonium nitrate in excess, ethyl ether and suitable internal standards were added and the extract was analyzed by GC. Naphthalene (**7**) and 1-phenylsulfanylnaphthalene (**8**) were identified in the reaction mixture by use of authentic samples.

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Supporting Information Available: General methods and ^{1}H NMR and ^{13}C NMR spectra of compounds **2a**, **3c**, and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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