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Highly Efficient Two-Step Synthesis of C-sp^3-Centered Geminal Diiodides

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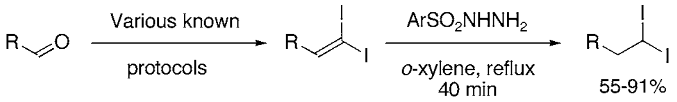
ABSTRACT



Trisubstituted *gem*-diiodoalkenes of functionalized chains are efficiently reduced to the corresponding terminal geminal diiodides in high yields upon treatment with the diazene precursor, diethyl 4-(hydrazinosulfonyl)-benzyl phosphonate.

Geminal diiodides ($RCHI_2$ where R is aryl or alkyl) are precursors to various organometallic intermediates that can be used as novel reagents to produce carbon−carbon bonds.[1] It is extremely difficult to find an adequate substitute for *gem*-diiodo compounds due to their unique reactivity. In contrast, the use of functionalized *gem*-diiodo compounds remains scarce in synthesis,[2] mainly due to the lack of suitable methods to access them when other functional groups are present in a substrate.

Their usefulness in mechanistic investigations and their synthetic potential have generated much interest in the preparation of compounds containing *gem*-diiodides centered on an sp^3 carbon. This area of research extends from Myers's recent contribution[3] to the pioneering work of Letsinger and Kammeyer[4b] five decades ago. Synthetic methods in which the oxidation state of the carbon is preserved[3,4] or increased[5] have shown low compatibility with functional groups and usually require uncommon reagents in addition to the need for tedious purification techniques. Presently, the most widely used method is that involving the alkylation reaction of CHI_2Li with highly electrophilic partners (primary halides or cyclic sulfates) since the reaction temperature has to be kept quite low to avoid carbene formation.[6] Isolation of the

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(1) For leading references of selected topics, see below. Diastereoselective cyclopropanation via $R_1CHI(ZnEt)$, see: (a) Schöllkopf, U.; Groth, U.; Tiller, T. *Liebigs Ann. Chem.* **1991**, 857−860. (b) Sugimara, T.; Katagiri, T.; Tai, A. *Tetrahedron Lett.* **1992**, *33*, 367−368. Enantioselective synthesis of allenes via $R_1CHI(ZnBu)$, see: (c) Varghese, J. P.; Zouev, I.; Aufauvre, L.; Knochel, P.; Marek, I. *Eur. J. Org. Chem.* **2002**, 4151−4158. Diastereo-, enantioselective cyclopropanation via $(R_1CHI)_2Zn$, see: (d) Charette, A. B.; Lemay, J. *Angew. Chem.*, Int. Ed. *Engl.* **1997**, *36*, 1090−1092. Catalytic diastereo-, enantioselective cyclopropanation via $(R_1CHI)_2Zn$, see: (e) Denmark, S. E.; Christenson, B. L.; O'Connor, S. P; Murase, N. *Pure Appl. Chem.* **1996**, *68*, 23−27. (*E*)-Olefination via $R_1CH(CrX)_2$, see: (f) Okazoe, T.; Takai, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 951−953. Diastereoselective cyclopropanation via $R_1CHI(SmI)$, see: (g) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1987**, *52*, 3942−3944. Diasteroselective alkylation of aldehydes via $R_1CHI(SmI_2)$, see: (h) Matsubara, S.; Yoshioka, M.; Utimoto, K. *Angew. Chem.*, Int. Ed. *Engl.* **1997**, *36*, 617−618. Diastereo-, enantioselective epoxidation via $R_1CHI(MgCl)$, see: (i) Schulze, V.; Hoffmann, R. W. *Chem.*—*Eur. J.* **1999**, *5*, 337−344. *o*-Alkylation of a phenol via $R_1CHI(ZnEt)$, see: (j) Lehnert, E. K.; Sawyer, J. S.; MacDonald, T. L. *Tetrahedron Lett.* **1989**, *30*, 5215−5218.

(2) For cyclopropanation using CH_3CHI_2, see: (a) Liu, P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 10772−10773. Olefination using $C_2H_5CHI_2$, see: (b) Stragies, R.; Blechert, S. *J. Am. Chem. Soc.* **2000**, *122*, 9584−9591. Olefination using $C_{13}H_{27}CHI_2$, see: (c) Johnson, D. V.; Felfer, U.; Griengl, H. *Tetrahedron* **2000**, *56*, 781−790. Olefination using $(MeO)_2CH(CH_2)_5CHI_2$, see: (d) Rechka, J. A.; Maxwell, J. R. *Tetrahedron Lett.* **1988**, *29*, 2599−2600.

(3) Furrow, M. E.; Myers, A. G. *J. Am. Chem. Soc.* **2004**, *126*, 5436−5445.

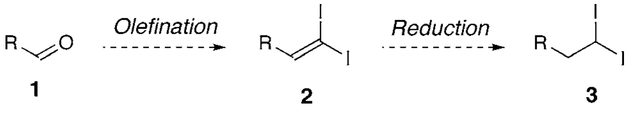
(4) From geminal dichloride. Use of $FeCl_3$, see: (a) Miller, J. A.; Nunn, M. J. *Tetrahedron Lett.* **1974**, *15*, 2691−2694. Use of $AlCl_3$, see: (b) Letsinger, R. L.; Kammeyer, C. W. *J. Am. Chem. Soc.* **1951**, *73*, 4476−4476. Use of AlI_3, see: (c) Anson, C. E.; Sheppard, N.; Powell, D. B.; Norton, J. R.; Fisher, W.; Keiter, R. L.; Johnson, B. F. G.; Lewis, J.; Bhattacharrya, A. K.; Knox, S. A. R.; Turner, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 3058−3062. From an aldehyde. Use of P_2I_4, see: (d) Feshchenko, N. G.; Kondratenko, N. V.; Yagupol'skii, L. M.; Kirsanov, A. V. *Zh. Org. Khim.* **1970**, *6*, 190−190. Use of TMSI, see: (e) Jung, M. E.; Mossman, A. B.; Lyster, M. A. *J. Org. Chem.* **1978**, *43*, 3698−3701. Use of Tf_2O/MgI_2, see: (f) Garcia Martinez, A.; Herrera Fernandez, A.; Martinez Alvarez, R.; Garcia Fraile, A.; Bueno Calderon, J.; Osio Barcina, J. *Synthesis* **1986**, 1076−1078. From a triple bond, see: (g) Aufauvre, L.; Marek, I.; Knochel, P. *Chem. Commun.* **1999**, 2207−2208. From a diazo, see: (h) Neuman, R. C. Jr.; Rahm. M. L. *J. Org. Chem.* **1966**, *31*, 1857−1859. See also: (h) Pross. A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989−1003.

(5) Gonzalez, C. C.; Kennedy, A. R.; Leon, E. I.; Riesco-Fagundo, C.; Suarez, E. *Angew. Chem., Int. Ed.* **2001**, *40*, 2326−2328.

10.1021/ol047997l CCC: \$27.50

gem-diiodide from residual CH_2I_2 or the electrophile is not always possible. Furthermore, the compounds containing *gem*-diiodides are often highly unstable[7] and can easily undergo decomposition via the free carbene.[8] In this communication, we describe an efficient new mild route to functionalized *gem*-diiodides. The method involves the transformation of a carbonyl **1** into a *gem*-diiodoalkene[9] **2** that is then chemoselectively reduced under metal-free reduction (Scheme 1).

Scheme 1. General Approach to 1,1-Diiodoalkanes

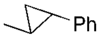
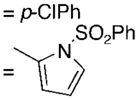
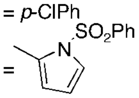


1 **2** **3**

Previous examples involving the reduction of *gem*-dihaloalkenes are limited to the specific case of *gem*-difluoro- and dichloroalkenes that were reduced upon treatment with H_2 and Pd/C.[10] We avoided harsh reduction conditions with metal catalysts due to the sensitivity of both the starting alkene and the resulting *gem*-diiodide. A wide range of *gem*-diiodalkenes **2** were synthesized from aldehydes **1** (Scheme 2). The reductant "diazene" (HN═NH) that can be generated in several ways, including one that has been reported to be suitable to reduce alkynes with no over-reduction of a carbon−iodine bond (Table 1, entry 4).[11] After extensive experimentation to find an efficient set of conditions (Table 1),[11] we were pleased to discover that the decomposition of arylsulfonohydrazide is a suitable approach for the reduction of diiodoalkene **2f**. When the decomposition was promoted

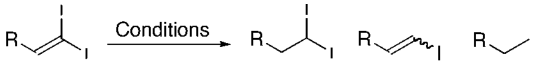
Scheme 2. Synthesis of 1,1-Diiodoalkenes[a]

1 **2**

1a R = *n*-Hex	**2a** R = *n*-Hex	***C***
1b R = $(CH_2)_2Ph$	**2b** R = $(CH_2)_2Ph$	***C***
1c R = 	**2c** R = 	***CE***
1d R = *c*-Hex	**2d** R = *c*-Hex	***C***
1e R = $C(Me)_2(CH_2)_2OBn$	**2e** R = $C(Me)_2(CH_2)_2OBn$	***C***
1f R = $(CH_2)_3OBn$	**2f** R = $(CH_2)_3OBn$	***ABCE***
1g R = CH_2NHCbz	**2g** R = CH_2NHCbz	***B***
	2h R = $(CH_2)_3OH$	***F***
1i R = $(CH_2)_4Cl$	**2i** R = $(CH_2)_4Cl$	***C***
1j R = $(CH_2)_2SO_2$*p*-Tol	**2j** R = $(CH_2)_2SO_2$*p*-Tol	***C***
1k R = $(CH_2)_4CO_2Et$	**2k** R = $(CH_2)_4CO_2Et$	***B***
1l R = $(CH_2)_3OPiv$	**2l** R = $(CH_2)_3OPiv$	***B***
1m R = $(CH_2)_4OTiPS$	**2m** R = $(CH_2)_4OTiPS$	***C***
	2n R = $(CH_2)_4CN$	***F***
1o R = $(CH_2)_2C(Me)_2NO_2$	**2o** R = $(CH_2)_2C(Me)_2NO_2$	***B***
1p R = $(CH_2)_3CHS(CH_2)_3S$	**2p** R = $(CH_2)_3CHS(CH_2)_3S$	***B***
1q R = Ph	**2q** R = Ph	***D***
1r R = *p*-ClPh	**2r** R = *p*-ClPh	***D***
1s R = 	**2s** R = 	***D***
1t R = Thienyl	**2t** R = Thienyl	***D***
	2u R = $(CH_2)_3I$	***F***

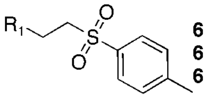
[a] For experimental details, see Supporting Information. Methods used for the synthesis of geminal diiodoalkenes: **A**: PPh_3, CI_4, DCM, rt, 2.5 h, 87%. **B**: PPh_3, CHI_3, *t*-BuOK, PhMe, −20 °C, 10−30 min, 37−69%. **C**: $(EtO)_2P(O)CH_2I$, I_2, LiHMDS, −78 °C, 10 min, 33−79%. **D**: $(EtO)_2P(O)CHI_2$, LiHMDS, THF, −78 °C, 10 min, 62−87%. **E**: $(EtO)_2P(O)Me$, I_2, LiHMDS, THF, −78 °C, 10 min, 46%. **F**: Multistep routes, see Supporting Information.

Table 1. Survey of Conditions for the Reduction of Geminal Diiodoalkene **2f**



2f **3f** **4f** **5f**

entry	conditions[a]	results[b] **2f/3f/4f/5f/6f**
1	H_2, Pd/C (10%), AcOEt, (1 atm)	100/0/0/0/0
2	H_2, Pd/C (10%), AcOEt, (6 atm)	100/0/0/0/0
3	$NaBH_4$, $NiCl_2(H_2O)_6$, $EtOH/Et_2O$	0/0/0/100/0
4	$KO_2CN_2CO_2K$, AcOH/MeOH, Py, rt	95/5/0/0/0
5	$KO_2CN_2CO_2K$, AcOH/MeOH, Py, reflux	90/5/5/0/0
6	$KO_2CN_2CO_2K$, AcOH/MeOH, reflux	90/5/5/0/0
7	NH_2OH, KOH, DMF, reflux	100/0/0/0/0
8	NH_2NH_2, H_2O_2, rt	*dec*
9	NH_2NH_2, H_2O_2, -78 °C	100/0/0/0/0
10	NH_2NH_2, O_2, $CuSO_4$	100/0/0/0/0
11	2,4,6 *i*-$PrC_6H_2SO_2N_2H_3$, AcONa, H_2O/THF, reflux	100/0/0/0/0
12	2,4,6 *i*-$PrC_6H_2SO_2N_2H_2$, H_2O/THF, reflux	100/0/0/0/0
13	*o*-$NO_2C_6H_4SO_2N_2H_3$, $NH_2CH_2CH_2OH$, MeOH, rt	96/2/2/0/0
14	*p*-$MeC_6H_4SO_2N_2H_2$, AcONa, H_2O/THF, reflux,1 h	91/7/0/0/2
⇨15	*p*-$MeC_6H_4SO_2N_2H_3$, AcONa, H_2O/THF, reflux, 24 h	50/30/0/0/20
16	*p*-$MeC_6H_4SO_2N_2H_3$, K_2CO_3, H_2O/THF, reflux, 24 h	*dec*
⇨18	*p*-$MeC_6H_4SO_2N_2H_3$, $MeOCH_2CH_2OH$, reflux, 1.5 h	68/32/0/0/0



6f $R_1 = (CH_2)_2CH_2OBn$
6k $R_1 = (CH_2)_3CH_2COOEt$
6l $R_1 = (CH_2)_2CH_2OPiv$

[a] See Supporting Information. [b] ^1H NMR of crude mixture.

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(6) Displacement of primary halides by $LiCHI_2$, see: (a) Charreau, P.; Julia, M.; Verpeaux, J. N. *Bull. Soc. Chim. Fr.* **1990**, *127*, 275−282. Ring opening of cyclic sulfates by $LiCHI_2$, see: (b) Stiasny, H. C.; Hoffmann, R. W. *Chem.—Eur. J.*. **1995**, *1*, 619−624. Use of CHI_3 as source of a "CI_2" unit, see: (c) Baker, R.; Castro, J. L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 47−65. (d) Seyferth, D.; Lambert, R. L. Jr. *J. Organomet. Chem.* **1973**, 54, 123−130. See also: (e) Christoph, G. G.; Fleischer, E. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 600−603.

(7) Decomposition and/or β-elimination proceed upon exposure for hours to H_2O_2, pyridine, HCl, or NaOH in water. β-Elimination with DBU, see: Garcia Martinez, A.; Martinez Alvarez, R.; Martinez Gonzalez, S.; Subramanian, R. L.; Conrad, M. *Tetrahedron Lett.* **1992**, *33*, 2043−2044.

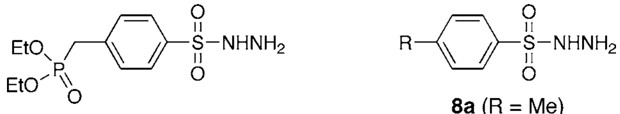
(8) Using $h\nu$ irradiation, see: (a) Miranda, M. A.; Perez-Prieto, J.; Font-Sanchis, E.; Scaiano, J. C. *Acc. Chem. Res.* **2001**, *34*, 717−726. See also: (b) Pienta, N. J.; Kropp, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 655−657. Using LAH, see: (c) Ashby, E. C.; Deshpande, A. K. *J. Org. Chem.* **1994**, *59*, 3798−3805.

(9) For selected references for the synthesis of trisubstituted *gem*-diiodoalkenes, see: (a) Gaviña, F.; Luis, S. V.; Ferrer, P.; Costero, A. M.; Marco, J. A. *J. Chem. Res., Miniprint* **1986**, 2843−2852. (b) Dabdoub, M. J.; Dabdoub, V. B.; Baroni, A. C. M. *J. Am. Chem. Soc.* **2001**, *123*, 9694−9695. (c) Bonnet, B.; Le Gallic, Y.; Plé, G.; Duhamel, L. *Synthesis* **1993**, 1071−1073.

by NaOAc (Table 1, entry 14), the desired *gem*-diiodide **3f** was obtained along with a sulfonylated byproduct **6f**. When *gem*-diiodoalkenes **2l** and **2k** were submitted to the reduction, the corresponding byproducts **6l** and **6k** were generated.

We eventually found that thermal decomposition of commercially available 4-methylbenzenesulfono hydrazide in refluxing 2-methoxyethanol (bp 124 °C) gave an encouraging conversion (Table 1, entry 18). It is widely accepted that diazene decomposes during the reduction process as soon as it is formed and that it may reduce the alkene through a pericyclic six-membered ring-type transition structure.[12] Sulfinic acid byproduct undergoes a known thermal rearrangement to afford compounds that are often difficult to separate from the desired alkane.[12a,13,14a] To solve this purification problem, many have used a polymer-supported arylsulfonohydrazide[14] or polymer-supported alkenes.[14b,15]

We opted to modify the reagent by introducing a polar substituent at the para position to allow easy removal of the byproducts. We eventually found that the introduction of a diethylphosphonate group[16] on the aryl moiety of the reagent led to a compound with the desired properties. Furthermore, this phosphonate does not interfere in the reduction process, and a simple filtration of the cooled reaction mixture through a pad of silica gel afforded the desired diiodo compound without any residual sulfur-containing byproducts. The efficiency of **7** as a reducing agent was compared with reagents **8a**−**c** (Table 2). The variation of the para substituent on the aryl group of the reagent had little effect on the level of conversions of **2f** into **3f** as long as this group was compatible with the reducing conditions.

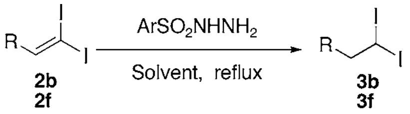


7

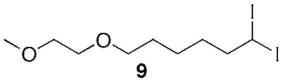
8a (R = Me)
8b (R = H)
8c (R = NO_2)

Figure 1. Arylsulfonohydrazide derivatives.

Table 2. Preparation of Geminal Diiodides via the Reduction of Geminal Diiodoalkenes Using **7**



entry	product	$ArSO_2NHNH_2$ (equiv)	concn (mol/L)	t (min)	conversion[a]
1[b]	**3f**	**8a** (1)	0.078	90	32
2[b]	**3f**	**8a** (2)[i]	0.078	90	57
3[b]	**3f**	**8a** (4)[i]	0.078	90	50[m]
4[b]	**3f**	**8b** (1)	0.078	90	40
5[b]	**3f**	**8c** (1)	0.078	90	44
6[b]	**3f**	**7** (1)	0.078	90	34
7[b]	**3f**	**7** (1)	0.156	90	42
8[b]	**3f**	**7** (1)	1.0	90	47
9[c,d]	**3f**	**7** (1)	1.0	10	36
⇨10[b]	**3f**	**7** (6)[j]	0.156	540	>95
⇨11[b]	**3b**	**7** (6)[j]	0.156	540	>95
12[e]	**3b**	**7** (1)	0.156	10	26
13[e]	**3f**	**8a** (1)	1.0	10	43
14[e]	**3f**	**7** (1)	1.0	10	54
15[e,f]	**3f**	**7** (1)	1.0	10	36
16[e,g]	**3f**	**7** (1)	1.0	10	46
17[e]	**3b**	**7** (1)	1.0	10	56
18[h,d]	**3b**	**7** (1)	1.0	10	56
19[e]	**3b**	**7** (1)[k]	1.0	40	56
⇨20[e]	**3b**	**7** (4)[l]	1.0	40	>95
21[e]	**3b**	**7** (1)	2.0	10	65
⇨22[e]	**3b**	**7** (4)[l]	2.0	40	>95



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[a] Determined by ^1H NMR of the crude reaction mixture. [b] 2-Methoxyethanol was used as the solvent. [c] 2-Methoxyethyl ether was used as the solvent. [d] Reaction was run at 162 °C. [e] *o*-Xylene was used as solvent. [f] Reaction was run in a sealed tube with microwave irradiation at 144 °C. [g] Reaction was run in a sealed tube with microwave irradiation at 162 °C. [h] 1-Methylnaphthalene was used as the solvent. [i] Added in one portion. [j] To the mixture was added 1 equiv of the reagent every 90 min. [k] To the mixture was added 0.25 equiv of the reagent every 10 min. [l] To the mixture was added 1 equiv of the reagent every 10 min. [m] Decomposition was observed by ^1H NMR.

In 2-methoxyethanol, reagent **8a** was slightly less effective in comparison with the parent compound **8b** (entry 1 vs 4). Conversely, the corresponding reagent **8c** bearing a *p*-NO_2 group gave a conversion slightly higher than with **8b** (entry 4 vs 5). Although the conversion with **7** was slightly lower than those observed with **8b** and **8c** (entry 6), we were confident that we could improve the yield by increasing the number of equivalents of the reagent. It is also worth mentioning that 2-methoxyethanol could be substituted for 2-methoxyethyl ether (entry 9), *o*-xylene (entries 12 and 17), or 1-methylnaphthalene (entry 18). This solvent modification is especially useful for substrates that are potentially sensitive to nucleophilic solvents. Further optimization led us to establish suitable conditions to obtain the desired *gem*-diiodides **3b** and **3f** in 78 and 76% yield. High conversions were observed for both substrates when using 4−6 equiv of sulfonohydrazide **7** (entries 10, 11, 20, 22). However, the portionwise addition of the reducing agent was proven to be crucial. Much lower conversions were observed if the

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(10) For *gem*-dichloroalkene, see: (a) Blinn, R. C.; Gunther, F. A. *J. Am. Chem. Soc.* **1950**, *72*, 1399−1401. For *gem*-difluoroalkene, see: (b) Kitazume, T.; Ohnogi, T; Miyauchi, H.; Yamazaki, T. *J. Org. Chem.* **1989**, *54*, 5630−5632.

(11) For ref see Supporting Information.

(12) Leading references, see: (a) Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271−280. (b) Pasto, D. J.; Taylor, R. T. *Org. React.* **1991**, *40*, 91−155. Theorical studies for the outcome of diazene, see: (c) Pasto, D. J.; Chipman, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 2290−2296. (d) Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6852−6857. (e) Tang, H. R.; McKee, M. L.; Stanbury, D. M. *J. Am. Chem. Soc.* **1995**, *117*, 8967−8973.

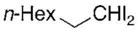
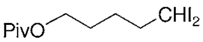
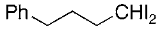
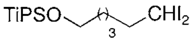
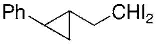
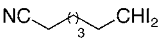
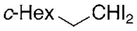
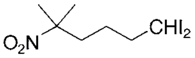
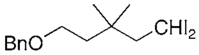
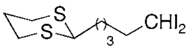
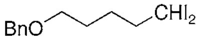
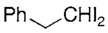
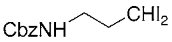
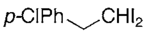
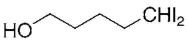
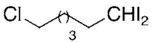
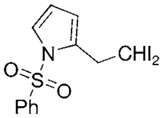
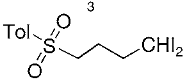
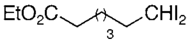
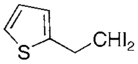
(13) Dewey, R. S.;Van Tamelen, E. E. *J. Am. Chem. Soc.* **1961**, *83*, 3729−3729.

(14) (a) Emerson, D. W.; Emerson, R. R.; Joshi, S. C.; Sorensen, E. M.; Turek, J. E. *J. Org. Chem.* **1979**, *44*, 4634−4640. (b) Gaviña, F.; Gil, P.; Palazón, B. *Tetrahedron Lett.* **1979**, *20*, 1333−1336.

(15) (a) Lacombe, P.; Castagner, B.; Gareau, Y.; Ruel, R. *Tetrahedron Lett.* **1998**, *39*, 6785−6786. (b) Nang, T. D.; Katabe, Y.; Minoura, Y. *Polymer* **1976**, *17*, 117−120.

(16) For the synthesis, see: (a) Herweh, J. *J. Org. Chem.* **1966**, *31*, 4308−4312. For blowing agent properties by thermal decomposition, see: (b) Herweh. J. U.S. Patent 3761544, 1973.

Table 3. Preparation of Geminal Diiodides via the Reduction of Geminal Diiodoalkene Using **7**[a]

product	yield (%)[b]	product	yield (%)[b]
	81 (**3a**)		81 (**3l**)
	89 (**3b**)		79 (**3m**)
	83 (**3c**)		55 (**3n**)
	87 (**3d**)		75 (**3o**)
	71 (**3e**)		72 (**3p**)
	80[c] (**3f**)		82 (**3q**)
	79 (**3g**)		76[d] (**3r**)
	87 (**3h**)		
	82 (**3i**)		77[d] (**3s**)
	91 (**3j**)		
	79 (**3k**)		61[d,e] (**3t**)

[a] Typical procedure: *gem*-dihaloalkene **2a**–**t** and sulfonohydrazide **7** (1 equiv) were heated under reflux for 10 min in *o*-xylene (1.0 M). An additional 3 equiv of **7** was added in 3 portions over 30 min. The mixture was cooled to room temperature, filtered through a pad of silica gel, and concentrated, affording pure material by ^{1}H NMR. [b] Isolated yield of analytically pure 1,1-diodoalkane. [c] Yield obtained was 75% when performed on a 3 g scale. [d] Up to 8% of the monoiodide was observed. [e] Conversion = 85%.

reagent was not added portionwise over a long period of time. The reaction could also be run at relatively high concentration (entries 9, 14, 20 and 22).

This optimal set of reaction conditions was then applied to several 1,1-diiodoalkenes to illustrate the generality of the reaction and its functional group tolerance under the relatively mild reducing conditions (Table 3). The generation of a *gem*-diiodide in the presence of Cbz-protected primary amines (**3g**), unprotected alcohols (**3h**), ethers (**3e**, **3f**), sulfones (**3j**), esters (**3k**, **3l**), pyrroles (**3s**), thienyl groups (**3t**), nitro groups (**3o**), nitriles (**3n**), and chlorides (**3i**) is very effective under the reaction conditions, and high yields of the desired products were obtained. Alkenes or alkynes are obviously among the groups that are not compatible under these reducing conditions. Although 2-methoxyethanol could be used as the solvent for this reaction, it was not suitable for substrates bearing silyl protecting groups (**2m**) since these were cleaved under the reaction conditions. Attempts to reduce a substrate containing a primary iodine (**2u**) led to a S_N2 reaction of this group by the solvent (**9**). *gem*-Diiodides bearing relatively acidic β-protons were surprisingly stable (**3r**, **3s**), and β-elimination (and subsequent reduced monoiodide) products were observed only in small quantities.

In conclusion, an alternative and practical route to synthetically useful terminal *gem*-diiodides was described. The unprecedented reduction of *gem*-diiodoalkenes was performed using a novel *p*-substituted arylsulfonohydrazide reagent. The method shows excellent functional group compatibility, and high yields of the products were observed. The use of these precursors in the cyclopropanation reaction of alkenes is in progress and will be reported in due course.

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Supporting Information Available: Experimental procedures, characterization data, and spectra (^{1}H and ^{13}C NMR, IR, HRMS) for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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