A New Facile Synthesis of 1,1-Dibromo-2-arylethenes

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Received 23 May 2007

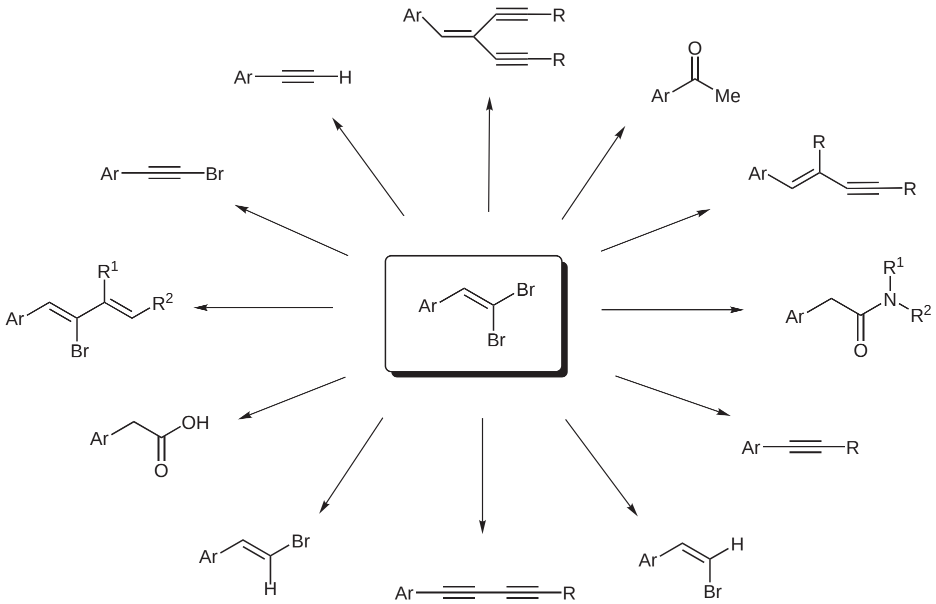
Abstract: Synthetically useful 1,1-dibromo-2-arylethenes were readily prepared in good yields via double bromodesilylation of the easily accessible 1,1-bis(trimethylsilyl)-2-arylethenes using *N*-bromosuccinimide under mild conditions.

Key words: 1,1-dibromo-1-alkenes, bromodesilylation, halogenation, organometallic reagents, silicon derivatives

1,1-Dibromo-2-arylethenes are valuable synthetic tools in organic chemistry. They can serve as precursors for the preparation of aryl acetamides,[1a] aryl acetic acids,[1b,c] amidines,[1b] 1-bromo-1-alkynes,[2] terminal alkynes (Corey–Fuchs protocol),[3] aryl methyl ketones,[4] etc. In addition, 1,1-dibromo-2-arylethenes have been largely employed as substrates for the stereoselective synthesis of geometrically pure (*E*)-[5] and (*Z*)-β-bromostyrenes.[6] Geminal dibromostyrenes can be also used as equivalents of (*Z*)-1-aryl-1-bromo-1-alkenes[7a,b] and (*Z*)-2-bromo-1,3-butadienes[7c] in Pd-catalyzed coupling reactions. Moreover, it is well established that the stereospecific palladium-catalyzed cross-coupling of 1,1-dibromo-2-arylethenes in a sequential manner provides access to configurationally defined trisubstituted alkenes such as triarylethenes,[2b] 2-aryl-1,1-dialkynylethenes[8a,b] or (*E*)-3-methyl-3-en-1-ynes.[8c] 1,1-Dibromo-2-arylethenes can also be used as precursors to internal alkynes[2b] and both symmetric and unsymmetric 1,3-diynes[9] (Scheme 1).

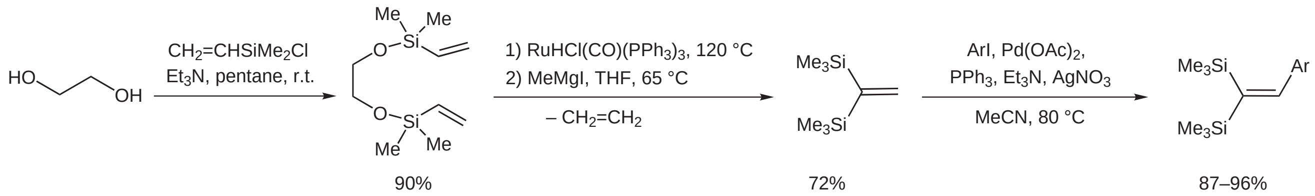
1,1-Dibromo-2-arylethenes are usually prepared by Wittig-type olefination of aryl aldehydes with triphenylphosphine and carbon tetrabromide.[3,10a] More recently, they have also been formed via tandem oxidation–Wittig reaction of activated benzyl alcohols[10b] or through the intermediacy of hydrazones.[10c] However, the necessity to use equimolar amounts of phosphoric reagents and/or carbon tetrabromide limits the appeal of these methodologies as a result of their toxicity.

Substituted styrylsilanes have been recognized as useful synthetic reagents since the carbon–silicon bonds are readily cleaved by various electrophiles in a regio- and stereoselective manner.[11] It was found that electrophilic bromination of these compounds proceeded with molecular bromine[12a–c] or *N*-bromosuccinimide (NBS)[12d,e] to give the corresponding styryl bromides or bis(2-bromoethenyl)arenes with retention of configuration. Although



Scheme 1

SYNLETT 2007, No. 13, pp 2061–2064
Advanced online publication: 17.07.2007
DOI: 10.1055/s-2007-984901; Art ID: G15407ST



Scheme 2

the utility of the 1-aryl-2-silylethenes as intermediates in the stereoselective synthesis of styryl bromides is well documented, the application of geminally silylated styrenes in the bromodesilylation process lags far behind mainly due to the complexity of their synthesis.

Recently we have developed a new facile and efficient protocol for the synthesis of 1,1-bis(silyl)-2-arylethenes from easily available starting materials using a sequential procedure: ethylene glycol silylation–one-pot deethenative silylative coupling cyclization[13a]/Grignard reagent treatment–Heck coupling[13b] (Scheme 2).

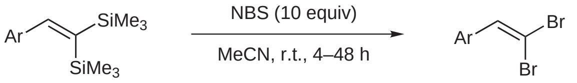
Having established a method for their selective synthesis and given synthetic utility of 1,1-dibromo-2-arylethenes we decided to explore the application of bromodesilylation procedure to 1,1-bis(trimethylsilyl)-2-arylethenes.

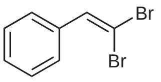
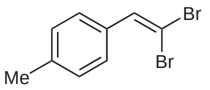
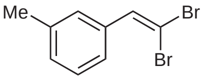
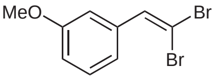
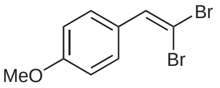
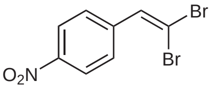
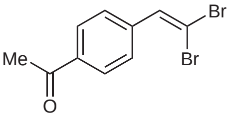
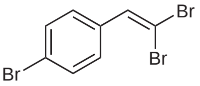
Initial studies were carried out with the 1,1-bis(trimethylsilyl)-2-phenylethene. After several attempts, we found that its reaction with NBS (10 equiv), conducted in anhydrous acetonitrile at room temperature for four hours exclusively afforded the bromodesilylation product, 1,1-dibromo-2-phenylethene in good (72%) yield (entry 1, Table 1).

To investigate the generality of this reaction, a series of 1,1-bis(silyl)-2-arylethenes bearing various substituents in the aromatic ring was subjected to similar reaction conditions. In a typical procedure, the 1,1-bis(silyl)-2-arylethene was dissolved in acetonitrile at room temperature and treated with ten equivalents of NBS.[14] In general, the reactions proceeded smoothly under mild conditions to give the corresponding β,β-dibromostyrenes in good yields, within 4–24 hours (Table 1).

In all cases, the monobromodesilylation of 1,1-bis(silyl)-2-arylethenes took place easily within one hour to form a mixture of two stereoisomeric 1-bromo-1-silyl-2-arylethenes (detected by GC–MS), however, the substitution of the second silyl group by bromine usually required a longer time (4–48 h) and an increase in the amount of NBS (from 5 equiv to 10 equiv per silyl group) did not appreciably affect the rate of this process. Moreover, in the cases of *m*-tolyl and *p*-tolyl substituted substrates (entries 2 and 3, Table 1), bromodesilylation was accompanied with the formation of the corresponding *m*- and *p*-bromomethyl derivatives (22% and 18% yields, respectively) via competitive bromination of the methyl substituents in the phenyl ring. However, they could be easily separated by column chromatography.

Table 1 Synthesis of 1,1-Dibromo-2-arylethenes via Bromodesilylation of 1,1-Bis(trimethylsilyl)-2-arylethenes[a]

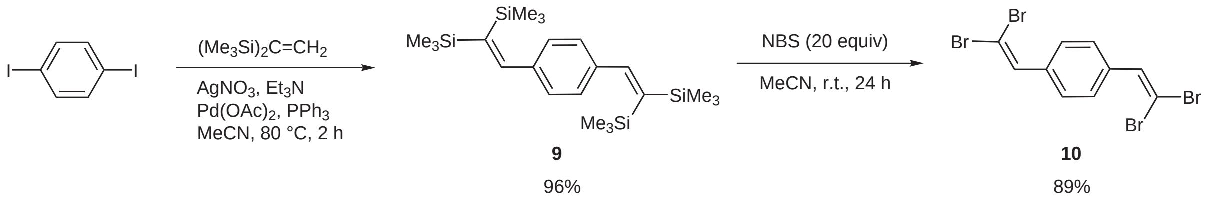


Entry	Ar	Time (h)	Product structure	Yield (%)[b]
1	Ph	4		72
2	*p*-MeC_6H_4	4		66
3	*m*-MeC_6H_4	4		68
4	*m*-$MeOC_6H_4$	24		88
5	*p*-$MeOC_6H_4$	24		82
6	*p*-$NO_2C_6H_4$	48		74
7	*p*-AcC_6H_4	24		90
8	*p*-BrC_6H_4	4		78

[a] Reactions performed on a 2-mmol scale with NBS (10 equiv) in MeCN (20 mL) at r.t.
[b] Isolated yields of chromatographically pure products.

It is worth noting that 1,1-bis(trimethylsilyl)-2-alkenylethenes, e.g. 1,1-bis(trimethylsilyl)-4-phenylbuta-1,3-diene under the same reaction conditions led to the selective formation of the dibrominated products containing 1,3-diene fragments.

As an extension to the present study we have found that our method can be also applied to the bromination of tetrasilyl derivative of 1,4-divinylbenzene,[15] easily obtained by Heck arylation of 1,1-bis(trimethylsilyl)ethene with 1,4-diiodobenzene (Scheme 3).[16]



Scheme 3

In conclusion, a new application of 1,1-bis(trimethylsilyl)-2-arylethenes to the synthesis of useful 1,1-dibromo-2-arylethenes via NBS-based bromodesilylation is described. Mild conditions, good functional group compatibility and the simplicity of the experimental technique of this new non-Wittig approach to 1,1-dibromo-2-arylethenes are favorable features of the reaction.

Acknowledgment

This work was made possible by a grant (PBZ-KBN 118/T09/17) from the Ministry of Science and Higher Education (Poland).

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(14) **A Typical Procedure for the Synthesis of 1,1-Dibromo-2-arylethenes and Spectroscopic Data of Selected Products**: *N*-Bromosuccinimide (3.55 g, 20 mmol) was added to the solution of the corresponding 1,1-bis(silyl)-2-arylethene (2 mmol) in anhyd MeCN (20 mL) and the suspension was stirred at r.t. for the appropriate time (see Table 1). The solvent was then evaporated and the mixture was extracted with *n*-hexane (50 mL). After extraction with an aqueous solution of $Na_2S_2O_3$ (5%, 50 mL) the organic layer was concentrated and the crude product was preloaded on to silica. 1,1-Dibromo-2-arylethenes were purified by silica chromatography, eluting with *n*-hexane–EtOAc (25:1).

1,1-Dibromo-2-(3-methoxyphenyl)ethene (4): yield: 0.514 g, 88%; yellowish oil. ^{1}H NMR ($CDCl_3$): δ = 3.86 (3 H, Me), 6.88–6.96 (m, 2 H), 7.30–7.34 (m, 1 H), 7.60 (s, 1 H, CH=), 7.68–7.72 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ = 55.2 (3 H, Me), 89.6 (=CBr_2), 110.3, 121.2, 124.2, 128.8, 129.9 (Ar), 132.8 (CH=), 156.4 (>COMe). MS (EI): *m/z* (%rel. int.) = 292 (56) [M^+], 277 (55), 210 (20), 168 (26), 132 (90), 117 (58), 102 (15), 89 (100), 74 (20), 63 (78). HRMS: *m/z* [M^+ + 2] calcd for $C_9H_8Br_2O$: 291.8922; found: 291.8916.

1,1-Dibromo-2-(4-nitrophenyl)ethene (6): yield: 0.454 g, 74%; yellow crystals; mp 105–106 °C. ^{1}H NMR ($CDCl_3$): δ = 7.55 (s, 1 H, CH=), 7.68 (d, *J* = 8.8 Hz, 2 H, Ar), 8.24 (d, *J* = 8.8 Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ = 94.3 (=CBr_2), 123.3, 129.1, 134.8 (Ar), 138.5 (CH=), 141.4 (>CNO_2). MS (EI): *m/z* (%rel. int.) = 307 (52) [M^+], 286 (78), 249 (20), 220 (25), 180 (25), 139 (95), 101 (54), 89 (30), 75 (100), 63 (20), 50 (34). HRMS: *m/z* [M^+ + 2] calcd for $C_8H_5Br_2NO_2$: 306.8667; found: 306.8654.

1,1-Dibromo-2-(4-acetylphenyl)ethene (7): yield: 0.547 g, 90%; yellowish crystals; mp 73–74 °C. ^{1}H NMR ($CDCl_3$): δ = 2.60 (3 H, Me), 7.68 (s, 1 H, CH=), 7.30 (d, *J* = 8.2 Hz, 2 H, Ar), 7.76 (d, *J* = 8.2 Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ = 28.9 (Me), 91.8 (=CBr_2), 128.0, 135.6, 147.7 (Ar), 148.9 (CH=), 153.3 (Ar), 196.3 (CO). MS (EI): *m/z* (%rel. int.) = 304 (25) [M^+], 289 (100), 261 (20), 180 (25), 129 (15), 101 (30), 75 (30), 50 (20). HRMS: *m/z* [M^+] calcd for $C_{10}H_8Br_2O$: 303.9779; found: 303.9786.

1,1-Dibromo-2-(4-bromophenyl)ethene (8): yield: 0.531 g, 78%; colorless oil. ^{1}H NMR ($CDCl_3$): δ = 7.60 (d, *J* = 8.6 Hz, 2 H, Ar), 7.52 (s, 1 H, CH=), 7.71 (d, *J* = 8.6 Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ = 90.2 (=CBr_2), 122.6, 129.8, 132.4, 134.1 (Ar), 135.6 (CH=). MS (EI): *m/z* (%rel. int.) = 341 (100) [M^+], 261 (45), 180 (60), 101 (46), 75 (48), 50 (40).

HRMS: *m*/*z* [M$^+$ + 2] calcd for $C_9H_5Br_3$: 339.7921; found: 339.7930.

(15) **Synthesis of 1,4-Bis(2,2-dibromoethenyl)benzene (10)**: *N*-Bromosuccinimide (3.55 g, 20 mmol) was added to the solution of 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene (0.418 g, 1 mmol) in anhyd MeCN (50 mL) and the suspension was stirred at r.t. for 24 h. The solvent was then evaporated and the mixture was extracted with *n*-hexane (50 mL). After extraction with aqueous solution of $Na_2S_2O_3$ (5%, 50 mL) the organic layer was concentrated and the crude product was preloaded onto silica. 1,4-Bis(2,2-dibromoethenyl)benzene was purified by silica gel chromatography, eluting with *n*-hexane–EtOAc (25:1) (0.397 g, 89%; white crystals; mp 108–109 °C). ^{1}H NMR ($CDCl_3$): δ = 7.39 (s, 2 H, CH=), 7.68 (s, 4 H, Ar). ^{13}C NMR ($CDCl_3$): δ = 90.4 (=CBr_2), 128.4, 132.3 (Ar), 136.2 (CH=). MS (EI): *m*/*z* (%rel. int.) = 446 (100) [M$^+$], 365 (12), 286 (30), 206 (18), 126 (48), 63 (25). HRMS: *m*/*z* [M$^+$] calcd for $C_{10}H_6Br_4$: 445.7162; found: 445.7176.

(16) **Synthesis of 1,4-Bis[2,2-bis(trimethylsilyl)ethenyl] benzene (9)**: A mixture consisting of palladium(II) acetate (67.0 mg, 0.30 mmol), triphenylphosphine (157.2 mg, 0.6 mmol), silver nitrate (1.70 g, 10 mmol), 1,4-diiodobenzene (5 mmol), 1,1-bis(trimethylsilyl)ethane (10 mmol, 1.72 g), triethylamine (2.80 mL, 20 mmol) and acetonitrile (30 mL) was placed in a 50-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil-bath at 80 °C for 2 h. After cooling to r.t., the reaction mixture was added to H_2O (50 mL) and extracted with pentane (2 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the crude product obtained was then purified by column chromatography (silica gel, pentane) to give the pure product (2.01 g, 96%) as white crystals. ^{1}H NMR ($CDCl_3$): δ = –0.01 (s, 18 H, SiMe), 0.18 (s, 18 H, SiMe), 7.12 (s, 4 H, Ar), 7.72 (s, 2 H, =CH). ^{13}C NMR ($CDCl_3$): δ = 0.5 (SiMe), 2.1 (SiMe), 127.4, 141.4 (Ar), 146.3 (CH=), 154.7 (>C=). MS (EI): *m*/*z* (%rel. int.) = 418 (10) [M$^+$], 345 (15), 257 (10), 171 (100), 131 (10), 73 (15). HRMS: *m*/*z* calcd for $C_{22}H_{42}Si_4$: 418.2363; found: 418.2348.