Tetrahedron Letters,Vol.25,No.12,pp 1219-1222,1984 0040-4039/84 $4.00 + .00
Printed in Great Britain

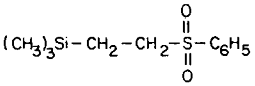
(E)- AND (Z)-1-BENZENESULFONYL-4-TRIMETHYLSILYL-2-BUTENES AS (E)-1-(1,3-BUTADIENYL) SYNTHONS

C-N. Hsiao and H. Shechter*

Chemistry Department, The Ohio State University, Columbus, Ohio 43210

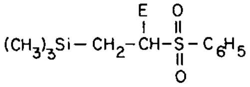
Abstract: (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (E/Z=9), prepared from 4-trimethylsilyl-1-buten-3-ol, *n*-butyllithium and benzenesulfenyl chloride and oxidation of the intermediate (E)- and (Z)-1-benzenesulfinyl-4-trimethylsilyl-2-butenes with hydrogen peroxide, react with *n*-butyllithium and then primary halides to give 4-benzenesulfonyl-1-trimethylsilyl-2-alkenes which are rapidly 1,4-debenzenesulfonyltrimethylsilated to (E)-1,3-alkadienes by tetra-*n*-butylammonium fluoride at 0^oC.

1-Benzenesulfonyl-2-trimethylsilylethane (1) is converted successively by *n*-butyllithium and various electrophiles to 1-benzenesulfonyl-1-substituted-2-trimethylsilylethanes (2) and 1-benzenesulfonyl-1,1-disubstituted-2-trimethylsilylethanes (3) via lithiated intermediates 4 and 5[1]. Of particular note is that 2 and 3 undergo efficient 1,2-debenzenesulfonyltrimethylsilation by tetra-*n*-butylammonium fluoride (1 equiv) to yield substituted-ethenes (6) and 1,1-disubstituted-ethenes (7), respectively, and thus 4 and 5 are operational vinyl anion (8) and vinylidene dianion (9) equivalents[1].



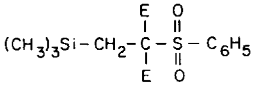
$(CH_3)_3Si-CH_2-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5$

1



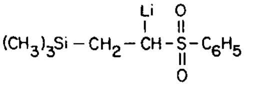
$(CH_3)_3Si-CH_2-\overset{\overset{E}{|}}{CH}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5$

2



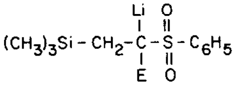
$(CH_3)_3Si-CH_2-\overset{\overset{E}{|}}{\underset{\underset{E}{|}}{C}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5$

3



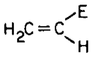
$(CH_3)_3Si-CH_2-\overset{\overset{Li}{|}}{CH}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5$

4

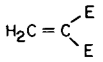


$(CH_3)_3Si-CH_2-\overset{\overset{Li}{|}}{\underset{\underset{E}{|}}{C}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5$

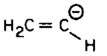
5



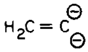
6



7



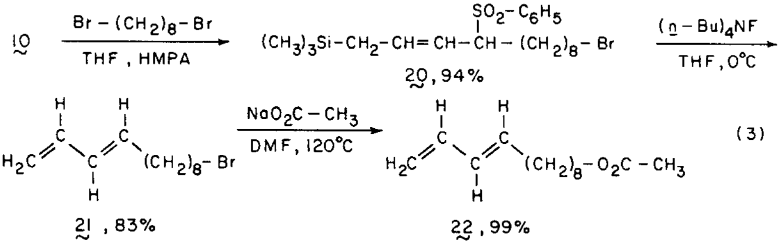
8



9

We now report (1) a practical synthesis of (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (10; E/Z ratio = 9), (2) the complete conversion of 10 to 11[2a] by *n*-butyllithium in tetrahydrofuran (THF) at -70^oC, (3) exclusive alkylation of 11 at C-1 by primary halides in THF/hexamethylphosphoric triamide (HMPA) at $20-25^oC$ to give 4-benzenesulfonyl-1-trimethylsilyl-2-alkenes (12) and (4) efficient 1,4-debenzenesulfonyltrimethylsilation (87-95%) of 12 by tetra-*n*-butylammonium fluoride (1 equiv) in THF at 0^oC via 13 to yield (E)-1,3-alkadienes (14, Eq 1). Preparation of 10 and its conversions to 14 under such mild conditions reveal the enormous synthetic potential of 11 as an (E)-1-(1,3-butadienyl) anion equivalent (15) for reaction with varied nucleophiles.

essentially total (E)-stereochemistry.[2c] A further example of the utility of 11 is synthesis of (E)-9,11-dodecadien-1-yl acetate (22), a sex pheromone of the red bollworm moth, as illustrated in Equations 3.[5]

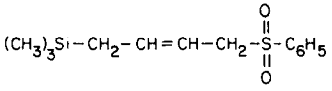


The preparative methods for 10-11 and 17-22 are described below. Study of the reactions of 11, its homologs and its analogs with varied electrophiles and the elimination reactions of the derivatives thereof is in progress.

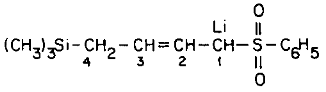
4-Trimethylsilyl-1-buten-3-ol (17). Acrolein (10 g, 178.6 mmol) in THF (10 mL) was added at 0°C to the Grignard reagent (16)[3] from chloromethyltrimethylsilane (20.0 g, 163.3 mmol) and magnesium (5.0 g, 205.6 mmol) in THF (150 mL). The resulting solution was stirred 40 min at 0°C, quenched with saturated ammonium chloride and washed with brine. The organic layer was dried ($MgSO_4$), filtered, concentrated and distilled at reduced pressure to give 17 (15.3 g, 106.2 mmol, 65%), a colorless liquid; bp 45-50°C/1.5mmHg; NMR (CCl_4, δ) 0.00 (s, 9H), 0.75-1.00 (m, 2H), 1.90 (bs, 1H), 4.25 (bq, 1H) and 4.90-6.15 (m, 3H); exact mass calcd for $C_7H_{16}SiO(M^+)$:144.2899; found: 144.2904.

1-Benzenesulfinyl-4-trimethylsilyl-2-butenes (19). Benzenesulfenyl chloride (15.0 g, 104.2 mmol) was added slowly to 17 (15.0 g, 104.2 mmol) and n-butyllithium (67 mL, 1.65M in hexane, 110.6 mmol) in THF (100 mL) at -70°C. The red color of the benzenesulfenyl chloride disappeared immediately. After 2 hr at room temperature, the colorless solution turned light yellow. The mixture was diluted with ethyl ether, washed with brine, dried ($MgSO_4$) and concentrated. Column chromatography (silica gel) of the residue with hexane and then benzene, elution with ethyl acetate and evaporation yielded 19 (24.9 g, 98.8 mmol, 95%, E/Z = 9), a light yellow oil; NMR (CCl_4, δ) 0.00 (s, 9H), 1.50 (bd, J = 8 Hz, 2H), 3.50 (bd, J = 8 Hz, 2H), 4.80-6.00 (m, 2H) and 7.30-7.70 (m, 5H); exact mass calcd for $C_{13}H_{20}SiSO(M^+)$ 252.1004; found: 252.1001.

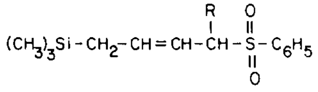
1-Benzenesulfonyl-4-trimethylsilyl-2-butenes (10). To 19 (20 g, 79.3 mmol) in dichloromethane (300 mL) at 0°C was added MCPBA (80-85% assay, 16.8 g, 77.9-82.7 mmol) in small portions. The white suspension was stirred at 0°C for 1 hr, filtered and concentrated. The residue was diluted with ethyl ether, washed with 25% aqueous sodium metabisulfite, aqueous sodium bicarbonate and brine, dried ($MgSO_4$), filtered and evaporated. The concentrate was diluted with benzene, pushed through silica gel and evaporated to 10 (18.5 g, 69.0 mmol, 87%, E/Z = 9), a colorless oil; NMR (CCl_4, δ) -0.10 (s, 9H), 1.45 (bd, J = 6 Hz, 2H), 3.70 (bd, J = 6 Hz, 2H), 5.10-5.60 (m, 2H) and 7.45-7.90 (m, 5H); exact mass calcd for $C_{13}H_{20}SiSO_2(M^+)$ 268.0953; found: 268.0956.


$(CH_3)_3Si-CH_2-CH=CH-CH_2-\overset{O}{\underset{O}{S}}-C_6H_5$

10

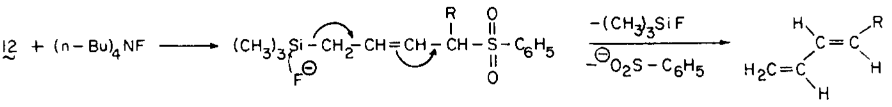

$(CH_3)_3Si-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\overset{Li}{CH}}-\overset{O}{\underset{O}{S}}-C_6H_5$

11

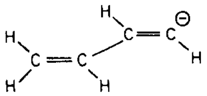

$(CH_3)_3Si-CH_2-CH=CH-\overset{R}{CH}-\overset{O}{\underset{O}{S}}-C_6H_5$

12

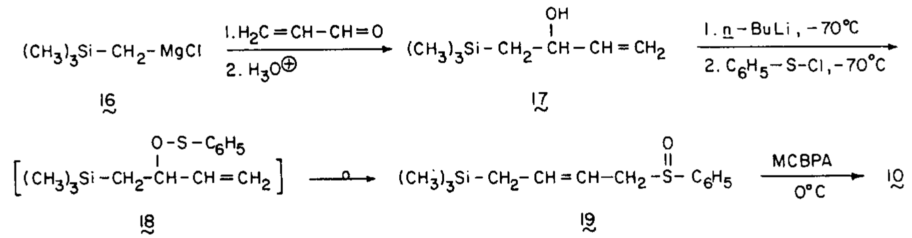
12a: $R=CH_3(CH_2)_4-$, 96% ; 12b: $R=CH_3(CH_2)_7-$, 90% ; 12c: $R=C_6H_5-CH_2-$, 91 %


13 14 (1)

14a: $R=CH_3(CH_2)_4-$, 83% ; 14b: $R=CH_3(CH_2)_7-$, 87 %; 14c: $R = C_6H_5-CH_2-$, 95%


15

Synthesis of 10 is accomplished readily (Eq 2) by (1) addition of trimethylsilylmethylmagnesium chloride (16)^3 to acrolein in THF at 0°C, acidification of the carbonyl adduct and distillation to yield 4-trimethylsilyl-1-buten-3-ol (17, 65%), (2) reaction of 17 in THF at -70°C with *n*-butyllithium (one equiv) and then benzenesulfenyl chloride (one equiv) to give (E)- and (Z)-1-benzenesulfinyl-4-trimethylsilyl-2-butenes (19, 95%, E/Z ratio = 9) by spontaneous rearrangement of the initial 4-trimethylsilyl-1-buten-3-yl benzenesulfenates (18) formed,^{4} and (3) oxidation (87%) of 19 with *meta*-chloroperbenzoic acid (MCPBA) in methylene chloride at 0°C. The overall sequence to 10 is straight-forward, efficient and adaptable to large scale operations.


(2)

Conversion of 10 in THF to 11 occurs rapidly at -70°C upon reaction with *n*-butyllithium/hexane. Addition of HMPA and then 1-iodopentane, 1-bromooctane and benzyl bromide results in 4-benzenesulfonyl-1-trimethylsilyl-2-nonenes (12a, 96%), 4-benzenesulfonyl-1-trimethylsilyl-2-dodecenes (12b, 90%) and 4-benzenesulfonyl-5-phenyl-1-trimethylsilyl-2-pentenes (12c, 95%), respectively^{2b}. 1,4-Elimination of 12a-c by tetra-*n*-butylammonium fluoride occurs in less than 20 min at 0°C to give 1,3-nonadiene (14a, 83%), 1,3-dodecadiene (14b, 87%) and 5-phenyl-1,3-pentadiene (14c, 95%), respectively, of

4-Benzenesulfonyl-12-bromo-1-trimethylsilyl-2-dodecene (**20**). *n*-Butyllithium (1.7 mL, 1.65M in hexane, 2.80 mmol) was syringed under nitrogen into **10** (0.7g, 2.61 mmol) in THF (15 mL) at -70°C. The light yellow solution was stirred 20 min and 1,8-dibromooctane 3.60g, 13.2 mmol) and then HMPA (2.5 mL) were added. The mixture was stirred 12 hr at ~25°C, diluted with ethyl ether, washed with water, dried, evaporated and column chromatographed (silica gel) with hexane and then benzene to yield **20** (1.13g, 2.46 mmol, 94%) as a colorless oil; NMR (CCl_4, δ) -0.30 (s, 9H), 0.80-2.05 (m, 16H), 3.20 (bt, J = 4 Hz, 2H), 3.30-3.70 (m, 1H), 4.60-5.60 (m, 2H) and 7.35-7.75 (m, 5H).

(E)-12-Bromododeca-1,3-diene (**21**). To **20** (1.0g, 2.18 mmol) in THF (10 mL) at 0°C was added tetra-*n*-butylammonium fluoride (5 mL, 1M in THF, 5 mmol). After 20 min the mixture was diluted with petroleum ether (35-60°C), washed with aqueous sodium bicarbonate, dried, and passed through silica gel. Evaporation yielded **21** (0.53g, 2.16 mmol, 99%), a colorless liquid: NMR (CCl_4, δ) 1.10-2.30 (m, 14H), 3.40 (t, J = 4 Hz, 2H), 4.85-5.35 (m, 2H) and 5.45-5.60 (m, 3H).

(E)-9,11-Dodecadien-1-yl Acetate (**22**). A suspension of **21** (0.50 g, 2.04 mmol) and anhydrous sodium acetate (5.0 g) in dimethylformamide (15 mL) was heated at 120°C for 10 hr. The mixture was cooled, diluted with ethyl ether (100 mL) and washed several times with water and saturated aqueous sodium bicarbonate. The organic phase, on drying and evaporation, yielded **22** (0.38g, 1.69 mmol, 83%); NMR (270 MHz, $CDCl_3$, δ) 1.20-1.70 (m, 12H), 2.05 (s, 3H), 2.10 (m, 2H), 4.05 (t, J = 6 Hz, 2H), 4.90-4.95 (d, J = 10 Hz, 1H), 5.05-5.10 (d, J = 17 Hz, 1H), 5.60-5.74 (dt, J = 15 Hz,[2d] 7 Hz, 1H), 5.95-6.10 (dd, J = 15 Hz, 10 Hz, 1H), and 6.20-6.35 (ddd, J = 17 Hz, 10 Hz, 10 Hz, 1Hz); exact mass calcd for $C_{14}H_{24}O_2(M^+)$ 224.1776; found: 224.1774.

Acknowledgement: This research was supported by the National Science Foundation.

References and Notes

1. (a) P. J. Kocienski, *Tetrahedron Lett.*, 2649 (1979). (b) P. J. Kocienski, *J. Org. Chem.*, **45**, 2037 (1980). (c) C.-N. Hsiao and H. Shechter, *Tetrahedron Lett.*, 1963 (1982). (d) C-N. Hsiao and H. Shechter, *ibid.*, 3455 (1982).
2. (a) The stereochemistry of **11** is presumed to be highly (E). The bonding of lithium at C-1 in **11** is for illustrative purposes. (b) **12a-c** are greater than 90% (E). (c) Olefins **14a-c** are assigned from IR and NMR data and by comparison with literature values. (d) The (E)-stereochemistry of **22** is clearly defined by the typical *trans* coupling of H at C_9 and C_{10}.
3. C. R. Hauser and C. R. Hance, *J. Am. Chem. Soc.*, **74**, 5091 (1952).
4. For examples and the mechanism of isomerism of allyl sulfenates to allyl sulfoxides, see P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4869 (1968).
5. For previous syntheses of **22**, see (a) B. F. Nesbitt, P. S. Beevor, R. A. Cole, R. Lester and R. G. Poppi, *Tetrahedron Lett.*, 4669 (1973); (b) S. Tanaka, A. Yasuda, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **97**, 3252 (1975); (c) J. H. Babler and M. J. Martin, *J. Org. Chem.*, **42**, 1799 (1977); (d) K. Mori, *Tetrahedron*, **30**, 3807 (1974); (e) T. Mandai, H. Yasuda, M. Kaito, J. Tsuji, R. Yamaoka and H. Fukami, *ibid.*, **35**, 309 (1979); (f) R. Rossi, A. Carpita, and M. G. Quirici, *ibid.*, **37**, 2617 (1981); and (g) G. R. Knox and I. G. Thom, *J. C. S. Chem. Commun.*, 373 (1981).

(Received in USA 4 January 1984)