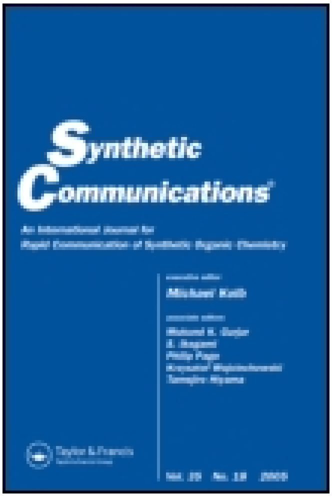

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Simple and Efficient Synthesis of the Acetylene Equivalent (E)-1-Benzenesulfonyl-2-(trimethylsilyl)ethylene

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SIMPLE AND EFFICIENT SYNTHESIS OF THE ACETYLENE EQUIVALENT (*E*)-1-BENZENESULFONYL-2-(TRIMETHYLSILYL)ETHYLENE

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Abstract: The acetylene equivalent (*E*)-1-benzenesulfonyl-2-(trimethylsilyl)ethylene is readily synthesized in a one-pot reaction, in excellent yield under very mild reaction conditions, *via* iodosulfonylation-dehydroiodination of vinyltrimethylsilane.

A great number of acetylene equivalents have been developed over the years for cycloaddition processes due to the low dienophilic reactivity and explosive nature of acetylene under pressure. The title compound (*E*)-1-benzenesulfonyl-2-(trimethylsilyl)ethylene **1** is one of them, perhaps the most elegant because post-cycloaddition reintroduction of the double bond involves very mild fluoride induced β-elimination of phenylsulfonyltrimethylsilane.[1] The versatility of **1** is based on its overall chemical behaviour which is a combination of the reactivities of both vinyl sulfones[2] and vinylsilanes.[3] Thus, sulfone **1** has been succesfully applied in a) Diels-Alder reactions[4] and anionic cycloadditions[5] acting as synthons **I**, **II** and **III**, b) in the synthesis of (*E*)-γ-hydroxyvinylsilanes[6]

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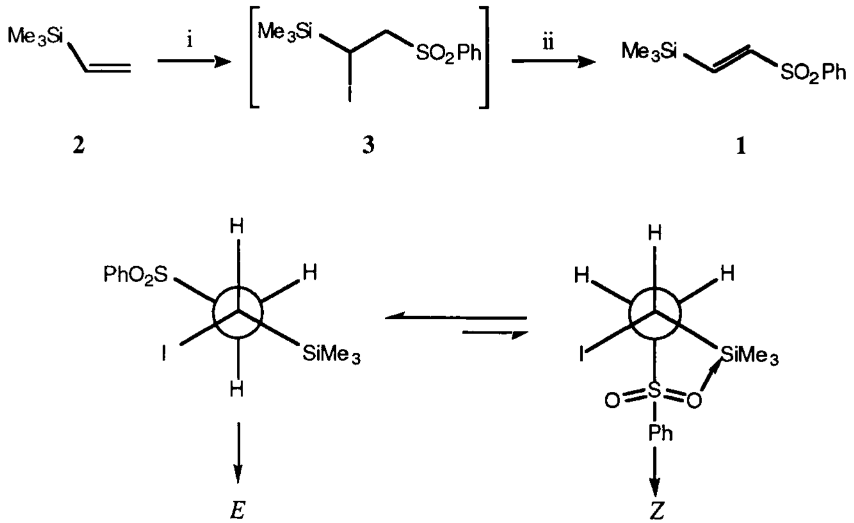
and c) as a precursor to allyloxysilanes[7a] and α-substituted allylsilanes.[7b]

$HC\equiv CH$ **I**

$RC\equiv CH$ **II**

$DC\equiv CH$ **III**

In this communication we report a simple and efficient one-pot synthesis of **1** *via* iodosulfonylation-dehydroiodination[8] of vinyltrimethylsilane **2** (Scheme 1).



Scheme 1. i, $I_2/PhSO_2Na/MeOH/0°C$. ii, $Et_3N/0\text{-}25°C$.

The advantages of this methodology are that the reagents are cheap and non-toxic,[6d,9] no catalysts or high pressures[4a,10,11] are required and the reaction can be conducted in one-pot.[12] A small amount of the Z-isomer is also obtained (*E*:*Z* ratio 8:1, ^{1}HNMR) in the dehydroiodination step but is readily separated by chromatography.

The Z-isomer arises from the sterically much more congested conformer which may reflect a weak interaction between one of the sulfonyl oxigen atoms and the trimethylsilyl moiety in the elimination transition state. The *E*/*Z*-product ratio is not altered at 0° and -20°C whilst inorganic bases such as NaOH, K_2CO_3 or NaOAc do not give good yields of alkene **1**.

In spite of the presence of two bulky groups, the non-isolated intermediate **3** undergoes nucleophilic substitution by phenylsulfinate anion at room temperature but fortunately this side reaction can be suppressed by working at 0°C.

EXPERIMENTAL.

(*E*)-1-Benzenesulfonyl-2-(trimethylsilyl)ethylene 1. Iodine (2.55 g, 10 mmol) was added in one portion to a stirred solution of sodium benzenesulfinate (1.64 g, 10 mmol) and vinyltrimethylsilane (0.8 ml, 5 mmol) in methanol (20 ml) cooled at 0°C. The mixture was stirred for 5h at 0-3°C when triethylamine (1.4 ml, 10 mmol) was added and stirring continued at room temperature for 2.5h. The solvent was evaporated under reduced pressure, the residue dissolved in dichloromethane (20 ml) and washed successively with 2N hydrochloric acid (10 ml) and 2M sodium thiosulfate (10 ml). The organic phase was dried (Na_2SO_4) and evaporated under reduced pressure affording product **1** (1.2g, quantitative yield of an 8:1 *E*:*Z*-mixture). The mixture was chromatographed on flash silica-gel eluting with *n*-hexane to afford the *E*-isomer **1** (0.86 g, 72%) and the *Z*-isomer[11] (0.11 g, 9%).

1 *[64489-06-1]*: Colourless needles, mp 58-59°C (lit.[11] 60°C) from *n*-hexane/ether. (Found: C, 55.25; H, 6.4; S, 13.3. $C_{11}H_{16}O_2SSi$ requires: C, 55.0; H, 6.7; S, 13.35%). δ_H(300MHz, $CDCl_3$) 0.15 (s, 9H, $3xCH_3$), 6.64, 7.25 (2xd, *J* 17.8 Hz, 2H, HC=CH), 7.52-7.64 (m with d at 7.57, *J* 7.7 Hz, 3H, ArH) and 7.89 (d, *J* 7.7 Hz, 2H, ArH). δ_C(75 MHz, $CDCl_3$) -2.41 (CH_3), 127.66, 127.89, 129.25, 133.41, 141.45 and 145.57 (ArC and C=C). *m/z* (EI, 70eV) 240 (M^+, 0.5%), 225 (22), 214 (29), 166 (26), 135 (54), 99 (12), 83 (22), 77 (44), 74 (16), 73 (100), 58 (21), 51 (28), 47 (27) and 43 (29). ν_{max} (film) 3060, 1660, 970 (C=C), 1300 and 1150 cm^{-1} (SO_2).

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