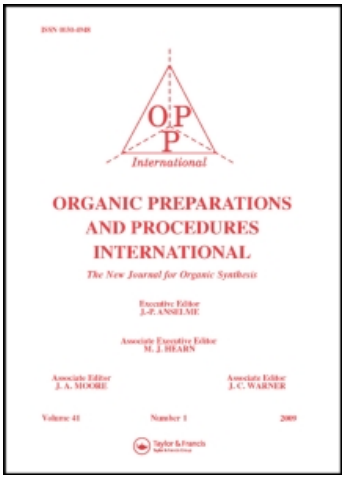

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A SIMPLE, EFFICIENT PREPARATION OF 1,1-BIS(TRIMETHYLSILOXY)-1,3-BUTADIENE

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A SIMPLE, EFFICIENT PREPARATION OF 1,1-BIS(TRIMETHYLSILOXY)-1,3-BUTADIENE

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(4/27/93)

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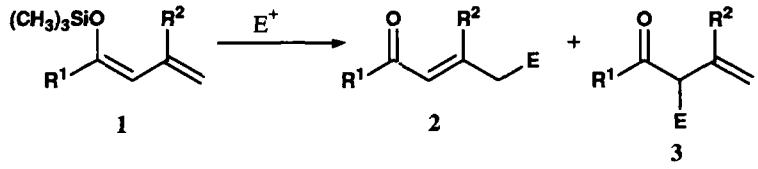
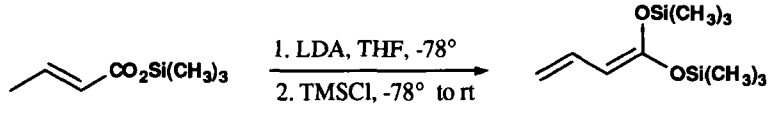
Ketene silyl acetals are frequently employed in organic synthesis as isolable ester enolate equivalents. These reagents are advantageous because they are easy to prepare and they exhibit higher reactivities toward electrophiles than the corresponding silyl enol ethers derived from ketones or thio esters.[1] Mukaiyama and Ishida reported the reaction of silyl dienol ethers with various electrophiles to afford the products resulting from attack at the γ-position (Eq. 1).[2] Fleming and co-workers later described that the γ-selectivity could be enhanced by increasing the size of R^1.[3]



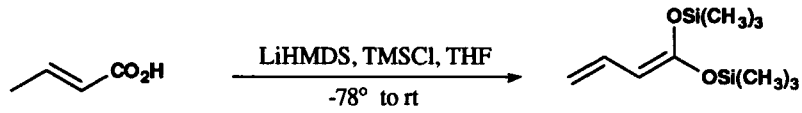
1 2 3 (1)

In comparison with the ester-derived *O*-silylated dienoates **1** (R^1 = OMe or OEt), 1,1-bis(trimethylsiloxy)-1,3-butadiene (**5**) should give higher γ-selectivity; however, its use has been quite limited, perhaps due to the absence of a simple, inexpensive preparation of this compound.[4] In 1983, Brady and Agho reported the first synthesis of 1,1-bis(trimethylsiloxy)-1,3-butadiene (**5**) in 9% yield from trimethylsilyl 2-butenoate (**4**) (Eq. 2).[5] Corresponding *C*-silylation proved to be a competitive reaction. More recently, Bellassoued and Majidi were able to prepare **5** in 90% yield by utilizing trimethylsilyl 3-butenoate as the starting material.[6]



4 5 (9%) (2)

In our laboratory, it has been observed that the use of a solution of lithium bis(trimethylsilyl)amide (LiHMDS) in the presence of TMSCl at -78°, led to the smooth conversion of *crotonic acid* (**6**) to 1,1-bis(trimethylsiloxy)-1,3-butadiene (**5**) in 70-77% yield (Eq. 3) without the complication of *C*-silylation.[7]



6 5 (70-77%) (3)

The procedure detailed here allows for the one-pot preparation of (**5**) in good yield from inexpensive, readily available starting materials.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer. The chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). Chlorotrimethylsilane (TMSCl) was distilled from calcium hydride under nitrogen, while tetrahydofuran (THF) was distilled under nitrogen from sodium/benzophenone. All other reagents and chemicals were purchased from common commercial suppliers and were used as received. Yields are not optimized.

Preparation of 1,1-Bis(trimethylsiloxy)-1,3-butadiene (5).- To a stirred, cooled (0°) solution of $(Me_3Si)_2NH$ (26 mL, 120 mmol) in THF (100 mL) was added a 2.5 *M* solution of *n*-BuLi in hexanes (49 mL, 120 mmol). The resulting solution was stirred at room temperature for 20 min and then cooled to -78°. To this solution was introduced freshly distilled TMSCl (15 mL, 120 mmol) dropwise over 5 min, followed by the dropwise addition of a solution of crotonic acid (**6**) (5.0 g, 58 mmol) in THF (20 mL) over 30 min. The reaction mixture was stirred for 2-5 hrs while gradually allowed to warm up to ambient temperature. The mixture was filtered quickly through Celite and the filtrate was concentrated under reduced pressure. The crude product was diluted in hexanes and again filtered quickly through Celite. The filtrate was concentrated and subsequent distillation afforded the known 1,1-bis(trimethylsiloxy)-1,3-butadiene (**5**) (9.4-10.3 g, 70-77%) as a colorless liquid, bp. 61-62°/1.0 mm Hg, lit.[7] bp. 42-44°/0.05 mm Hg. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (dt, J = 17.2, 10.5 Hz, 1 H, H3); 4.79 (dd, J = 17.2, 2.3 Hz, 1 H, H4); 4.57 (dd, J = 10.5, 2.5 Hz, 1 H, H4); 4.45 (d, J = 10.5 Hz, 1 H, H2); 0.26 (s, 9 H, $Si(CH_3)_3$); 0.22 (s, 9 H, $Si(CH_3)_3$).

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† American Cancer Society Postdoctoral Fellow 1993-1994 (PF-3868).

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A ONE-STEP PREPARATION AND HETERO-DIELS-ALDER DIMERIZATION OF 2-PHENYLPROPENAL

Submitted by (11/30/92)

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Atropaldehyde (2-phenylpropenal, **2**) is claimed to be an exocrine secretion compound of white cabbage butterfly *(Pieris rapae crusivora)*[1] and of ponerine and myrmicine ants.[2] The formation of **2** in the thermal degradation of polystyrene[3] and its reported instability under normal conditions led us to investigate its preparation and transformations.

The preparation of **2** was first reported in 1968.[4] Gas-phase catalytic oxidations of 2-phenylpropene (**1**)[5] is a patented process and the effects of various catalysts and reaction parameters have been studied recently.[6] Among laboratory scale methods,[7,8] the one reported by Crossland is adequate though involving three steps. We used the well-known ability of selenium dioxide to oxidize allylic positions[9] and obtained **2** in 44% yield from **1** in a 3 hrs reaction and distillation procedure.[10] Our method is rapid, uses less steps and gives a yield comparable to that of Crossland. Benzene turned out to be more suitable as a solvent than 1,4-dioxane or acetic acid.

Based on NMR and MS spectral evidence, it was found that **2** dimerizes to give a new pyran derivative, 2,5-diphenyl-2-formyl-3,4-dihydro-2H-pyran (**3**), *via* a hetero Diels-Alder reaction. HPLC