

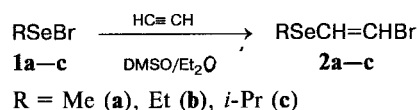
The first example of addition of alkylselenenyl bromides to acetylene

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Information on addition of alkylselenenyl halides to acetylenes is lacking, and rare examples involve only arylselenenyl halides.^{1,2} In some cases, depending on the solvent used, either *syn*- or *anti*-addition was observed.¹

We have studied for the first time the addition of alkylselenenyl bromides **1a–c** to acetylene. The reaction was found to be stereoselective. It proceeds at room temperature, with acetylene present under atmospheric pressure, to give the previously unknown (*E*)-alkyl(2-bromovinyl)selenides **2a–c** in a yield of up to 80%.



The bromides **1a–c** were prepared by adding an equimolar amount of bromine to an ethereal solution of the corresponding dialkyl diselenide. The ethereal solution of **1a–c** was added to DMSO saturated with acety-

lene, then acetylene was further passed through the solution for 5–7 h. The (*E*)-configuration of selenides **2a–c** was definitely proved by ¹H NMR spectroscopy (the coupling constant of vinyl protons is around 14 Hz).

Thus, a route has been found to valuable semi-products for organic synthesis, selenides **2a–c**, using a reaction which is quite simple from the experimental viewpoint. Various organoselenium compounds can be prepared on the basis of these products.

Below, the compound, yield, b.p. (°C/Torr), and *n*_D²⁰ are given: **2a**, 80, 50–52/10, 1.6157; **2b**, 77, 55–57/2, 1.6353; **2c**, 50, 66–68/2, 1.6563.

References

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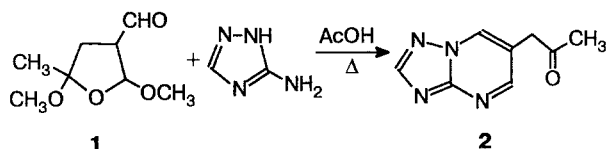
1,2,4-Triazolo[1,5-*a*]pyrimidines from 3-formyl-2,5-dimethoxytetrahydrofurans

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It is known that 3-formyl-2,5-dimethoxytetrahydrofuran interacts with primary amines to form 3-formylpyrroles.¹ We have found that 3-formyl-5-methyl-2,5-dimethoxytetrahydrofuran **1** when heated in acetic acid with 3-amino-1,2,4-triazole affords 6-(2-oxopropyl)-1,2,4-triazolo[1,5-*a*]pyrimidine **2** in 58% yield.

The aldehyde **1** was obtained for the first time by hydroformylation of 2-methyl-2,5-dimethoxy-2,5-dihydrofuran in the presence of Rh(acac)(CO)₂ + P(C₆H₅)₃ at 80°C. The yield was 79%, b.p. 76–78°C/5 Torr, *n*_D²⁰ 1.449.



A solution of 1.88 g of **1** and 0.91 g of 3-amino-1,2,4-triazole in 15 ml of glacial acetic acid was refluxed for 1.5 h. The mixture was cooled, concentrated *in vacuo*, and the residue was twice crystallized from alcohol to give 1.1 g of **2**, pale yellow prisms, m.p. 155°C. ¹H NMR spectrum (CDCl₃, δ, *J*, Hz): 2.4 (s, 3H, CH₃); 3.95 (d, 2H, CH₂); 8.48 (s, 1H, HC-(2)); 8.65 (d, 1H, HC-(5), ⁴*J* = 2.44); 8.8 (d, HC-7, ⁴*J* = 2.44). ¹³C NMR spectrum (DMSO-*d*₆, δ): 29.7 (CH₃); 42.6 (CH₂); 118.6 (C-6); 136.4 (C-7); 154.0 (N=C-N); 155.8 (C-5); 157.8 (C-2); 204.8 (C=O).

Reference

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