Liquid-phase thermal reactions of propargyl alcohol and its derivatives with dialkyl diselenides

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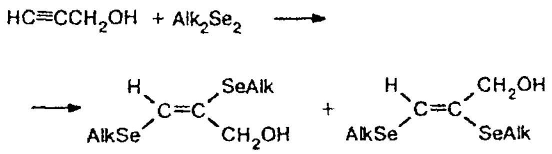
Heterocyclization with the formation of 1,2-diselenol-3-one (yield up to 73%) is the main direction of the gas-phase reaction (400—430 °C) of propargyl alcohol with dimethyl diselenide.[1]

We have found that liquid-phase reactions of dialkyl diselenides with propargyl alcohol occur in a different direction: heating of a mixture of propargyl alcohol and Alk_2Se_2 at 115—125 °C results in the formation of adducts **1** in the form of a mixture of *E*- and *Z*-isomers in 50—79% yield.



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Alk = Me, Et, Pr, Bu

The duration of the reaction depends substantially on the alkyl chain length in Alk_2Se_2: dimethyl and diethyl diselenides react within 13—14 h with 84 and 65% conversion, respectively. The 51—53% conversion of dipropyl and dibutyl diselenides is achieved only in 22 h. The yields of all compounds **1** calculated per consumed diselenide are approximately the same and equal to 87—96%. The ratio of *E*-/*Z*-isomers of **1** remains unchanged during the synthesis and depends weakly on the alkyl chain length.

If hydrogen atoms in propargyl alcohol are substituted by ethyl groups, this acetylenic alcohol reacts very slowly at 130—140 °C only with dimethyl diselenide to form an adduct of type **1** (after 12 h, the conversion of diselenide is 20%, and the yield of the adduct, according to the GLC data, reaches only 8.3%).

The reactions were performed by a slow introduction of the corresponding Alk_2Se_2 into propargyl alcohol taken in a double molar excess and heated to 110—115 °C. The course of the reaction was monitored by GLC, and compounds **1** were isolated by distillation *in vacuo* of the reaction mixtures.

1, Alk = Me, b.p. 112—118 °C (1 Torr). ^{1}H NMR, δ: 2.16, 2.15, 2.13 (all s, MeSe); 3.04 (br.s, OH); 4.3 (s, CH_2O, *E*-isomer); 4.18 (s, CH_2O, *Z*-isomer); 6.38 (s, CH=, *E*-isomer); 6.92 (s, CH=, *Z*-isomer); *E*/*Z* = 3/1.

1, Alk = Et, b.p. 148—157 °C (1 Torr). ^{1}H NMR, δ: 1.39 (t, Me, *E*-isomer); 1.43 (t, Me, *Z*-isomer); 2.73 (q, CH_2Se); 3.33 (br.s, OH); 4.26 (s, CH_2O, *E*-isomer); 4.19 (s, CH_2O, *Z*-isomer); 6.67 (s, CH=, *E*-isomer); 7.08 (s, CH=, *Z*-isomer); *E*/*Z* = 3.6/1.

1, Alk = Pr, b.p. 183—185 °C (1 Torr). ^{1}H NMR, δ: 1.00 (t, Me); 1.7 (m, C—CH_2—C); 2.71 (t, CH_2Se); 3.31 (br.s, OH); 4.26 (s, CH_2O, *E*-isomer); 4.18 (s, CH_2O, *Z*-isomer); 6.67 (s, CH=, *E*-isomer); 7.04 (s, CH=, *Z*-isomer); *E*/*Z* = 3.5/1.

1, Alk = Bu, b.p. 186—190 °C (1—2 Torr). ^{1}H NMR, δ: 0.96 (t, Me); 1.5 (m, C—$(CH_2)_2$C); 2.71 (t, CH_2Se); 3.31 (br.s, OH); 4.26 (s, CH_2O, *E*-isomer); 4.18 (s, CH_2O, *Z*-isomer); 6.66 (s, CH=, *E*-isomer); 7.04 (s, CH=, *Z*-isomer); *E*/*Z* = 3.5/1.

GLC analysis was carried out on an LKhM-8MD-2 chromatograph, stainless steel column (1000 × 3 mm), liquid phase DC 550, 15% on Chromaton N-AW, linear temperature-programmed regime (12 deg min^{-1}).

^{1}H NMR were recorded on a JEOL FX 90-Q instrument (90 MHz) for 15—20% solutions of substances in $CDCl_3$ (HMDS).

References

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