

UNUSUAL REACTION OF TRIALKYLSILYLALKANETHIOLS
WITH DIVINYL SULFOXIDE

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We discovered an unusual course for the reaction of trialkylsilylalkanethiols with the general formula $R_3Si(CH_2)_nSH$ (I), where $R = CH_3$ and C_2H_5 and $n = 2-3$, with divinyl sulfoxide (II) in the presence of bases. Instead of the expected nucleophilic addition of I to the $C=C$ bond of the sulfoxide (II), we observed the formation of 50-70% yields of vinyl trialkylsilylalkyl sulfides with the general formula $R_3Si(CH_2)_nSCH=CH_2$ (III).

tert-Butyl mercaptan (IV) reacted with II in a similar manner, and the yield of $(CH_3)_3CSCH=CH_2$ was about 17%. The main process in this case is the normal nucleophilic addition of IV to II to form (up to 70%) the monoadduct $(CH_3)_3CSCH_2CH_2SOCH=CH_2$. The sulfides were identified by IR spectroscopy and GLC with the use of standards obtained by a back synthesis [1]. The mechanism of the new reaction is under study.

A mixture of 12.2 g of II, 8.9 g of trimethylsilylpropanethiol, and 0.28 g of anhydrous KOH was heated for 2-3 h at 70°C. This yielded 6.2 g (59%) of vinyl trimethylsilylpropyl sulfide with bp 67°C (3 mm) and n_D^{20} 1.4970 (compare [2]).

In a similar manner vinyl triethylsilylpropyl sulfide (56%) with bp 87-88°C (3 mm) and n_D^{20} 1.4860 (compare [2]) and vinyl triethylsilylethyl sulfide (45%) were obtained from triethylsilylpropanethiol and triethylsilylethanethiol, respectively.

The following were obtained from 13.0 g of II, 5.76 g of IV, and 0.15 g of calcined KOH: a) 4.4 g (49%) of tert-butylthioethyl vinyl sulfoxide, bp 105°C (1 mm), d_4^{20} 1.0683. Found: C 46.89; H 8.21; S 35.45%. Calculated for $C_8H_{16}S_2O$: C 47.15; H 7.91; S 35.96%. b) 1.2 g (17%) of vinyl tert-butyl sulfide, bp 110°C (720 mm). Found: C 62.04; H 11.00; S 27.26%. Calculated for $C_6H_{12}S$: C 62.00; H 10.45; S 27.59%.

LITERATURE CITED

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