DIENE CONDENSATION OF DIVINYL SULFIDE WITH

 $\alpha$ ,  $\beta$ -UNSATURATED ALDEHYDES (SYNTHESIS OF SULFIDES

OF THE DIHYDROPYRAN SERIES)

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We have found that  $\alpha,\beta$ -unsaturated aldehydes react with divinyl sulfide to give adducts containing, depending on the conditions, one (I, II) or two (III) dihydropyran rings.

$$\begin{array}{c}
R \\
CH_2 \\
CH-S-CH
\end{array}$$

$$\begin{array}{c}
CH_2 \\
CH-S-CH
\end{array}$$

$$\begin{array}{c}
R \\
CH_2
\end{array}$$

$$\begin{array}{c}
R \\
CH_3
\end{array}$$

$$\begin{array}{c}
R \\
CH_3
\end{array}$$

Adduct I is capable of undergoing diene condensation with other 1,3-dienes; for example, it forms adduct IV with hexachlorocyclopentadiene:

The results of elementary analysis of I-III for C, H, and S and of IV for S and C1 coincide satisfactorily with the calculated values. 2-Vinylthio-3,4-dihydropyran (Ib), with bp 70° (10 mm),  $d_4^{20}$  1.0676, and  $n_D^{20}$  1.5270, was obtained in 47% yield. 2-Vinylthio-4-methyl-3,4-dihydropyran (II), with bp 50° (1 mm),  $d_4^{20}$  1.0259, and  $n_D^{20}$  1.5138, was obtained in 17% yield. The isomer ratio was 95:5. Bis(3,4-dihydropyran-2-yl) sulfide (III), with bp 82° (1 mm) and mp 36°, was obtained in 49% yield. 1,4,5,6,7,7-Hexachloro-2-(3,4-dihydropyran-2-yl)thio-bicyclo[2.2.1]heptene (IV), with bp 175° (0.5 mm), was obtained in 66% yield as viscous liquid that crystallized on standing. According to the results of gas-liquid chromatography (carried out with a 3-m long column with a diameter of 3 mm, polyphenyl ether on Chromaton N-AW-hexamethyldisiloxane, with helium as the carrier gas at a flow rate of 4 liters/h with a KhL-6 chromatograph with a thermal conductivity detector), the purity of I was no less than 96%. PMR spectrum,  $\delta$ , ppm (in CCl<sub>4</sub>): 6.13 (6-H, d,  $J_{65}$ =6.7 Hz,  $J_{64}$ =1.2 Hz), 5.16 (2-H, t,  $J_{23}$ =2.0 Hz), 4.71 (5-H, m), 2.04 (3-H, 3'-H, 4-H, 4'-H, and m), 6.60 (SCH, q), 5.32 (=CH, d,  $J_{CiS}$ =10.1 Hz), and 5.21 (=CH, d,  $J_{trans}$ =16.6 Hz). The isomerism of compounds of the II and IV type will be the subject of further study.

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