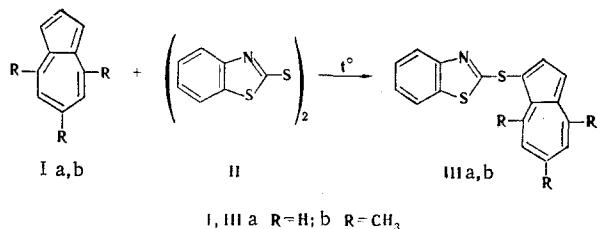


THERMAL REACTION OF AZULENES WITH
BENZOTHIAZOLYL DISULFIDE

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We have observed that heating azulene (Ia) or 4,6,8-trimethylazulene (Ib) with benzothiazolyl disulfide (II) is accompanied by the formation of the corresponding 1-azulenyl-2-benzothiazolyl sulfides (IIIa,b).



We assume radical substitution in the 1 position of the azulene ring (the site of highest electron density), since it is known that at high temperatures sulfide II is inclined to undergo homolytic cleavage to give benzothiazolylsulfenyl radicals. The structures of sulfides IIIa,b are confirmed by the results of elementary analysis (for C, H, N, and S) and the UV spectra. The known 1-phenylthio derivatives of azulene and 4,6,8-trimethylazulene absorb in the same spectral region as sulfides IIIa,b (the hypsochromic effect of the S-aryl groups in the 1 position of the azulene system causes a 20–25 nm shift of the absorption maximum to the short-wave region); this excludes substitution in the 2 position.

Thus 0.26 g of azulene was dissolved in 20 ml of ethylene glycol, 0.34 g of Altax was added, and the mixture was refluxed for 15 min. It was then cooled and treated with 400 ml of water, and the aqueous mixture was extracted with toluene. The extract was dried and chromatographed with a column filled with SiO₂; the violet zone was collected. The eluate was evaporated, and the residue (a violet oil) was triturated with ether to give 0.35 g (60%) of dark-violet needles of 1-azulenyl 2-benzothiazolyl sulfide (IIIa) with mp 70–72°C and R_f 0.41 (in benzene on Silufol), and λ_{max} (benzene) 560 nm ($\log \epsilon$ 2.68). 4,6,8-Trimethyl-1-azulenyl 2-benzothiazolyl sulfide (IIIb) was similarly obtained in 47% yield as bright-red crystals with mp 148–150°C (from n-heptane), R_f 0.36 (in benzene on Silufol), and λ_{max} (benzene) 530 nm ($\log \epsilon$ 2.88).

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