POLYHALOGEN-CONTAINING DISULPHIDES: SYNTHESIS AND FORMATION OF THIIRANES

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The investigation of the synthesis and reactivity of sulphur-containing organofluorine compounds revealed new polyhalogen-bearing disulphides. Symmetrical disulphides having halogen at β -position with respect to sulphur react with $P(\text{NEI}_2)_3$ to produce thiiranes, which depending on their structure are either final products (I) and (II) or undergo further conversions. The reaction probably proceeds via intermediate (A).

Thiirane (III), an analogue of (I) having CI in position 2, dehydrochlorinates to form an unstable (4n -electron antiaromatic) thiirene (IV) which dimerizes later.

$$(CF_3 - CCI - CH_2CI)_2 \xrightarrow{P(NEI_2)_3} \left[CF_3 - CCI - CH_2 \xrightarrow{-HCI} CF_3 - C = CH \right] \xrightarrow{CF_3} CF_3$$

$$(III) \qquad (IV)$$

The same reaction of disulphide (V) yields allene-episulphide (VI) which is a representative of a rather inaccessible class of exo-unsaturated thiiranes.

$$(CF_3) = C = C - CF_2 - CF_3)_2 \qquad P(NEI_2)_3 \qquad CF_3 = C - C - CF_3$$

$$CF_3 = C - CF_3 = CF_3$$

$$CF_3 = = CF_3$$

$$CF$$