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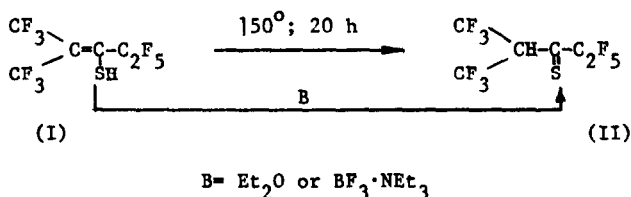
METASTABLE ENTHIOLS AND α,β -UNSATURATED SULPHENYL CHLORIDES. REARRANGEMENTS IN A TRIAD 'CARBON-CARBON-SULPHUR'

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As was shown for the first time, sterically unhindered tautomeric systems (enthiol-thioketone and α,β -unsaturated sulphenyl chloride-thioketone) with negligibly small rates of tautomeric conversions under normal conditions may be found among polyfluorinated monothiocarbonyl compounds. Metastable in these systems are respectively enthiols and α,β -unsaturated sulphenyl chlorides which are highly stable kinetically.

Enthiols and α,β -unsaturated sulphenyl chlorides do not convert spontaneously into the corresponding thioketones. However, basic catalysts or thermal treatment can isomerize enthiol (I) into thioketone (II). The reverse reaction cannot be carried out.



A tautomeric system - α,β -unsaturated sulphenyl chloride (III) + thioketone (IV) - in the presence of a weakly basic catalyst acquires a state of equilibrium with a low activation barrier of the form interconversions; in other words chlorotropy - migration of the chlorine in the triad 'carbon-carbon-sulphur' - is observed for the first time. In the absence of catalysts both forms are stable.

