HETEROCYCLES, Vol 21, No 2, 1984

FORMATION OF NOVEL 1,2-OXATHIETANES AND THEIR CHEMICAL REACTIVITY INCLUDING FORMAL $[\sigma 2_s + \sigma 2_a]$ CYCLOREVERSIONS AND REARRANGEMENT

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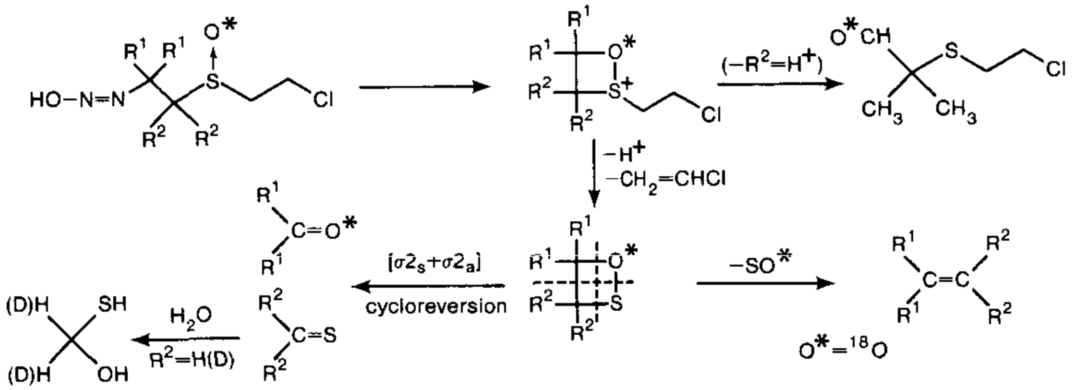
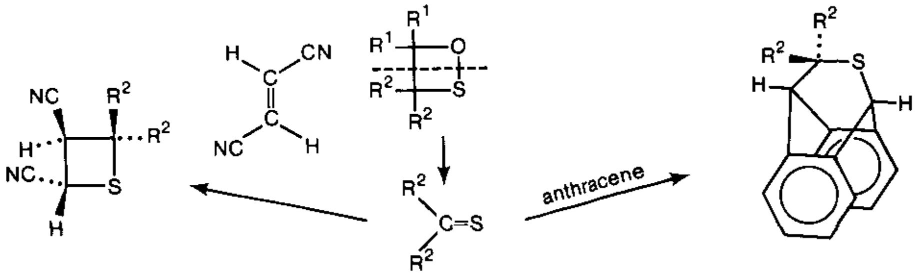
Aqueous decomposition of sulfinyl nitrosoureas at pH 7.0 and 37° via a diazohydroxide affords carbonyl and thiocarbonyl products which are in accord with formation of a novel 1,2-oxathietane which is subject to two alternative formal $[\sigma 2_s + \sigma 2_a]$ cycloreversions or ring opening to an aldehyde.



Experiments with the corresponding ^{18}O labeled sulfoxide confirms intramolecular oxygen transfer while parallel decompositions with specifically deuterium labeled nitrosoureas rule out the alternative pathway via a thiirane S-oxide. The thermally labile 3,3,4,4-tetramethyl-1,2-oxathietane, which is detectable by gas chromatography, undergoes (2+2) cycloreversion to acetone and thioacetone as well as loss of sulfur monoxide to give 2,3-dimethyl-2-butene. The reactive thiocarbonyl compounds may be trapped in [2+2] cycloadditions with e.g. fumaronitrile to give thietes or [2+4] cycloaddition with anthracene to afford bicyclothiole



derivatives. The synthetic potential of 1,2-oxathietanes for the preparation of sulfur heterocycles is being explored.