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### Syntheses of Novel Four Membered Rings Containing Oxygen and Sulphur as Heteroatoms

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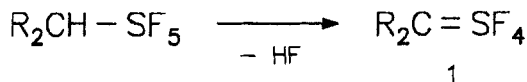
## SYNTHESES OF NOVEL FOUR MEMBERED RINGS CONTAINING OXYGEN AND SULPHUR AS HETEROATOMS

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**Abstract** The cyclisation of an alkylidenesulphur-tetrafluoride is shown. The addition of  $\text{SO}_3$  to  $\text{SF}_5$ -substituted olefins yields in an unexpected ring formation. The new oxadithietanes are presented and a mechanism for the formation is discussed. Ring opening of these compounds yields in the formation of new alkylidenesulphurdifluorideoxides.

### FORMATION OF AN OXATHIETE

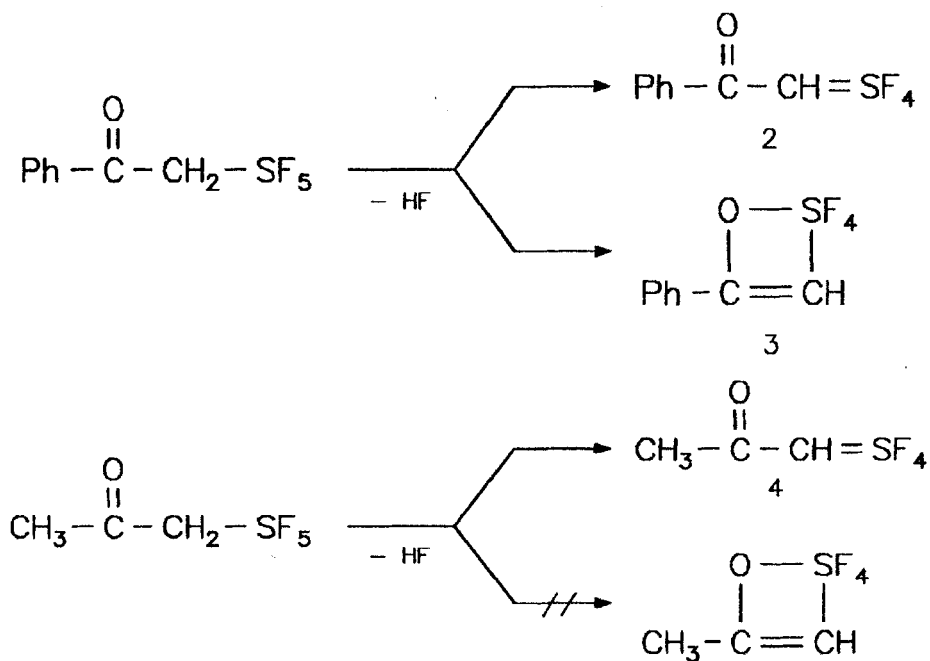
Alkylidenesulphurtetrafluorides (1) are formed if HF is eliminated from  $\text{SF}_5$ -substituted compounds.



HF elimination from  $\text{SF}_5$ -substituted acetophenone yields in the formation of two products. One is the expected alkylidenesulphurtetrafluoride (2) and the other one is identified by X-ray crystal analysis as the oxathiete (3)<sup>1</sup>.

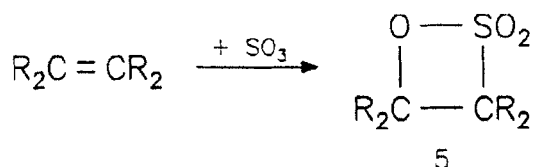
In the same reaction the  $\text{SF}_5$ -substituted acetone exclusively forms the noncyclic compound (4).

Factors upon which the ring formation depends on are still unclear.



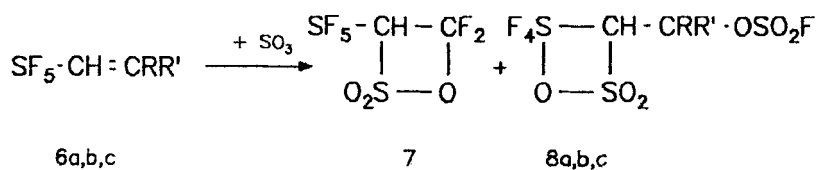
#### SYNTHESES OF OXADITHIETANES

$\text{SO}_3$  adds to olefinic double bonds in a [2+2]-cyclo-addition forming sultones (5).



There are several halogenated sultones known, but only two are substituted with a  $\text{SF}_5$ -group<sup>2) 3)</sup>. Sultone (7) is formed by the addition of  $\text{SO}_3$  to olefin (6a). We found that in this reaction not only sultone (7) is formed, but also a new compound, an oxadithietane (8a).

Other  $\text{SF}_5$ -substituted olefins (6b,c) react with  $\text{SO}_3$  to give exclusively the corresponding new products (8b,c).



a: R=R'=F

b: R=R'=H

c: R=F; R'=Cl

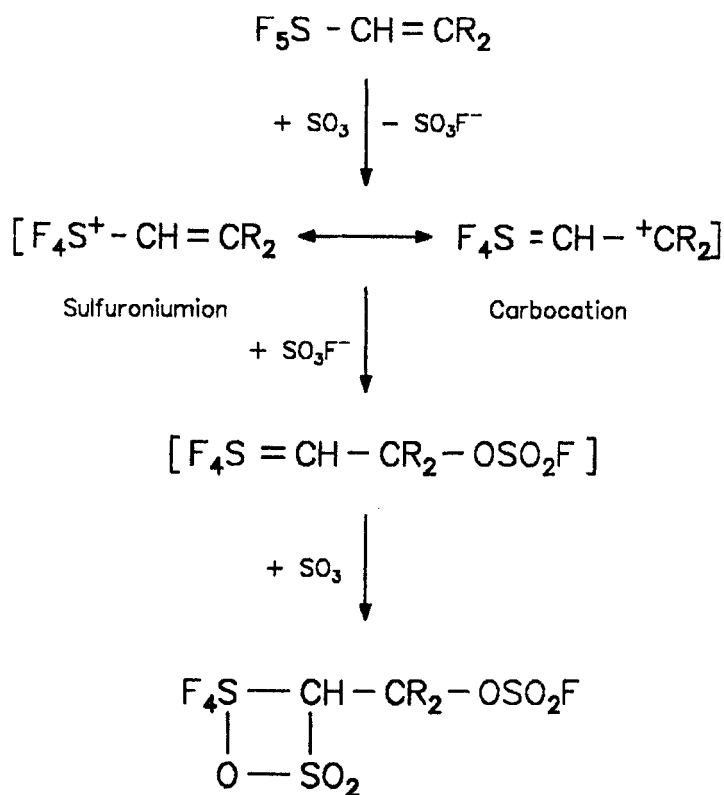
### MECHANISM FOR THE FORMATION OF OXADITHIETANES

An explanation for the unexpected formation of the oxadithietanes is required. A possible mechanism for this reaction is shown in scheme 1.

AsF<sub>5</sub> and SbF<sub>5</sub> react as strong Lewis acids with SF<sub>5</sub>-substituted alkanes by abstraction of a fluoride ion forming an sulfuronium cation (R-SF<sub>4</sub><sup>+</sup>) and the corresponding hexafluoride anion<sup>4</sup>).

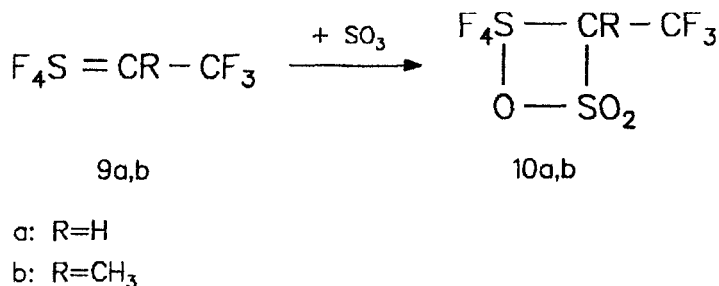
The Lewis acid SO<sub>3</sub> may also abstract a fluoride ion from SF<sub>5</sub>-substituted alkenes forming a fluorosulfate anion and a sulfuronium cation. The thus formed fluorosulfate anion then can react with the resonance stabilized carbocation forming an alkylidenesulphurtetrafluoride. The carbon-sulphur double bond can then react with another molecule of SO<sub>3</sub> to give the observed rings.

The proposed intermediate was not yet observed. This can be explained by rapid addition of the second molecule of SO<sub>3</sub> to the carbon-sulphur double bond.



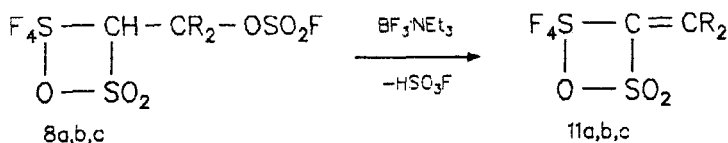
Scheme 1 Mechanism of the addition of  $\text{SO}_3$  to  $\text{SF}_5$ -substituted olefins

tetrafluorides (9a,b) to give the predicted oxadithi-  
etanes (10a,b).



#### SYNTHESES OF EXO-METHYLENE OXADITHIETANES

In the fluorosulfatomethylene substituted oxadithietanes (8a,b,c) the proton has an acidic character due to the electronwithdrawing effects of neighbouring substituents. The fluorosulfate group is also a good leaving group. Thus treatment with a base results in the elimination of fluoro-sulfonic acid to give oxadithietanes with an exocyclic carbon-carbon double bond, exo-methylene oxadithi-  
etanes (11a,b,c).

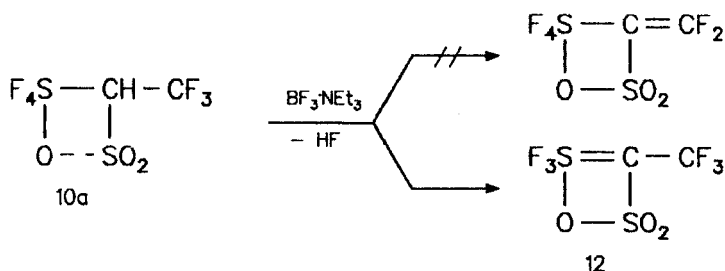


#### FORMATION OF AN OXADITHIETE

The success of this reaction prompted investigations into the removal of HF from the related CF<sub>3</sub>-substituted oxadithietane (10a).

Elimination of HF can occur to give two possible products, a saturated ring with an exocyclic carbon-carbon double bond or an unsaturated ring with a carbon-sulphur double bond within the ring.

The reaction was found to give exclusively the unsaturated ring, an oxadithiete (12). This new compound is the first example of a carbon sulphur double bond in a cyclic system.



The fluoride ion is eliminated from the sulphur atom because a sulphur-fluorine-bond is weaker than a carbon-fluorine-bond, and because the formation of an olefinic  $\text{CF}_2$ -group is energetically unfavorable.

A similar reaction is known from the previously shown sultone (7) where HF elimination forms also exclusively a carbon sulphur double bond instead of a carbon carbon double bond<sup>5)</sup>.

Such an unsaturated ring can also be considered a cyclic alkylidenesulphurtetrafluoride. In such compounds the sulphur has a trigonal-bipyramidal coordination with the carbon sulphur double bond in an equatorial position. This coordination of the sulphur atom can give two isomeric structural forms of an cyclic compound: The oxygen atom of the  $\text{SO}_3$ -group can either occupy an equatorial (fig. 1) or an axial position (fig. 2).

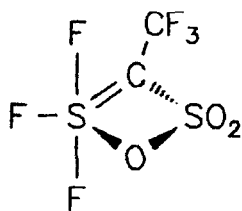


figure 1

Carbon and oxygen both  
in equatorial positions

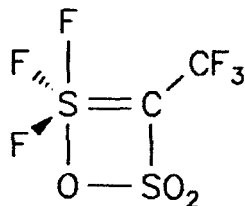


figure 2

Carbon in an equatorial, but  
oxygen in an axial position

The VSEPR-rules predict that the oxygen would be in an equatorial position because the more electronegative substituents, in this case the fluorine atoms, should occupy the axial positions. In this case the ring strain would be increased because a CSO-bond angle of approximately  $90^\circ$  is required instead of a normal bond angle of approximately  $120^\circ$  between the two equatorial positions.

If the oxygen occupies an axial position a CSO-bond angle of  $90^\circ$  is normally pretended. Thus by considerations of bond angles the oxygen atom would be predicted to occupy an axial position.

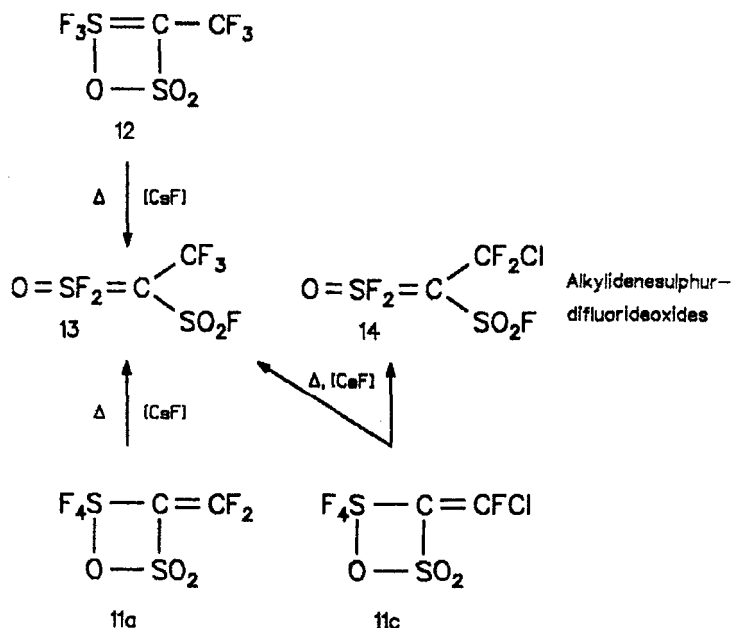
In the related non-cyclic compounds the two carbon substituents are in plane with the two axial fluorine atoms of the  $SF_4$ -group supporting the prediction that the oxygen will occupy an axial position.

The X-ray crystal structure of the oxadithiete (12) shows a planar four-membered ring in which the oxygen occupies an axial position contrary to the VSEPR-rules. It also shows a short carbon sulphur double bond of 157 pm contrary to the carbon sulphur single bond of 171 pm.



SYNTHESES OF NEW ALKYLIDENESULPHURDIFLUORIDEOXIDES

Alkali fluorides such as CsF catalyse the migration of fluoride ions. So heating of the oxadithiete (12) with a catalytic amount of CsF results in ring opening and a 1,3-fluoride migration to give the alkylidenesulphurdifluoride oxide (13).



The exo-methylene oxadithietanes (11a,c) undergo the same reaction with CsF, whereas compound (11c) forms not only the expected product (14), but also compound (13).

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