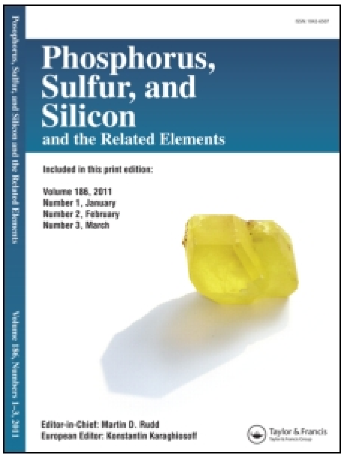

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Intermediates in Spirosulfurane Formations

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INTERMEDIATES IN SPIROSULFURANE FORMATIONS

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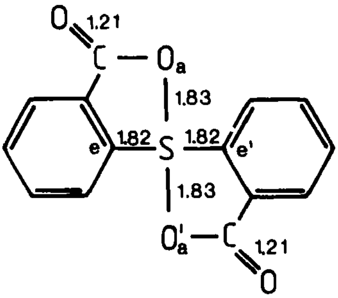
Abstract Spirosulfuranes can generally be prepared from the corresponding sulfides with halogenating agents or from sulfoxides by intramolecular dehydration. Mechanisms for the formations have been suggested and determined earlier (1979). Recently, intermediates in spirosulfurane formations have been prepared in our laboratory with molecular structures determined by X-ray diffraction methods. The molecular structures obtained are more compatible with the sulfonium salt formula than with the sulfuranium one, although the arrangement of the ligands about the sulfonium center can be described with a slightly or considerably distorted trigonal bipyramidal geometry due to the relatively strong $S^{\oplus}\cdots O$(carbonyl) interactions.

INTRODUCTION

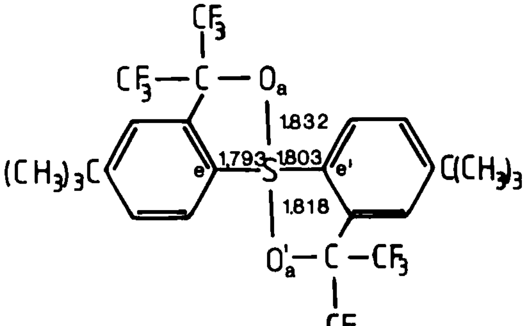
Spirosulfuranes can formally be derived from the hypothetic SH_4 molecule by replacement of hydrogenes by bidentate ligands. In these compounds - similarly to other sulfuranes - four ligands and the lone pair of electrons ("phantom ligand") are attached to the tetravalent sulfur in trigonal bipyramidal (TBP) spatial arrangement. The more electronegative ligands are in the axial, the other two and the lone pair are in equatorial positions.

The syntheses and molecular structures for the first representatives of S(IV)[C,C,O,O] type of spirosulfuranes were reported by us^{1a,b} for 1 and by Martin and coworkers^{2a-c} for 2 between 1971 and 1974. The compound 1 represents a diaryldiacyloxy-, while the compound 2 a diaryldialkoxy-type of spirosulfurane. It is interesting to note that both of these spirosulfuranes, especially 2 are relatively stable toward heating and hydrolysis.^{1a,2a}



1

$O_a{-}S{-}O'_a$ 178.5,
$C_e{-}S{-}C'_e$ 107.8°

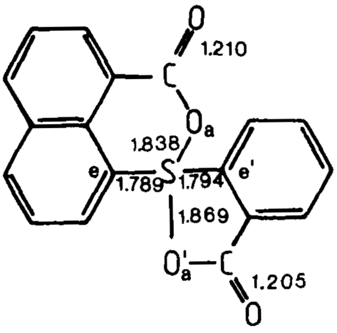


2

$O_a{-}S{-}O'_a$ 177.7,
$C_e{-}S{-}C'_e$ 107.9°

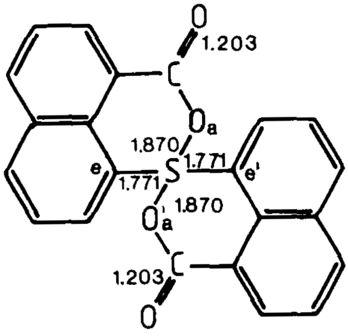
The molecular structures can be described with a slightly distorted TBP geometry about the sulfur, where the axial S-O bonds are considerably longer than the sum of the sulfur and oxygen covalent radii^{3} (1.70 Å), while the equatorial S-C ones are practically "normal" (sum of covalent radii^{3} 1.80 Å). The axial bond angles are near to the ideal 180°.

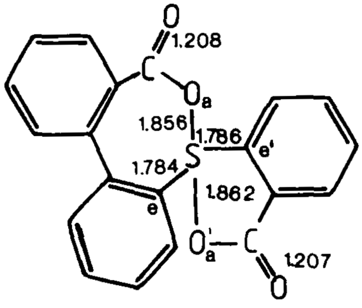
In order to obtain additional information about how the size of spirorings influence the molecular structures and chemical properties for this type of compounds, we have recently prepared diaryldiacyloxy spirosulfuranes with five-, six- and seven-membered rings and determined their molecular structures.[4] These spirosulfuranes (3, 4 and 5) having acyloxy groups at



3

	3	4	5
$O_a-S-O'_a$	176.7°	174.9°	175.7°
$C_e-S-C'_e$	105.8°	106.9°	105.9°





4 **5**

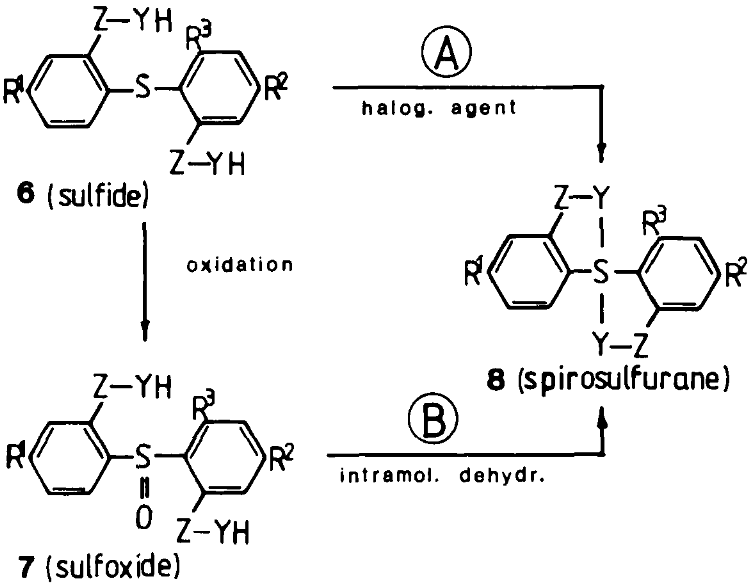
axial positions possess structures analogous to spirosulfurane 1.

Comparing the geometric parameters about sulfur we see that the corresponding data are very close both to each other and to those found for spirosulfurane 1 and 2. Thus, it may be assumed that the structural parameters about sulfur, in diaryldiacyloxy spirosulfuranes of S(IV)[C,C,O,O] type with five-, or six-, or seven-membered rings are not considerably influenced by the size of the spirorings.

To a first approximation, the structural data in the investigated molecular structures of spirosulfuranes can be interpreted on the basis of Musher's hypervalent bonding system theory.[5a-c] Accordingly, a three-center four-electron bond system is assumed in the axial directions constructed from the collinear *p*-orbitals of sulfur and oxygen, with only two electrons on the bonding MO, whereas the other two are on the nonbonding MO. The hybride orbitals of the equatorial bonding system are constructed from 3s, $3p_x$ and $3p_y$ atomic orbitals of the sulfur. The consequences are: the elongations of the axial bonds and the fact that these bonds are very polarized or polarizable, associated with negative charges at axial positions and with the positive charge on the central sulfur. Thus, it also becomes understandable that the more electronegative ligands are always in axial positions.

SYNTHESES, MECHANISMS AND INTERMEDIATES

Spirosulfuranes can generally be prepared from the corresponding sulfides (6) with halogenating agents[6] (e.g. Cl_2, Br_2, *t*-BuOCl, chloramine-T, dichloramine-T), or from sulfoxides (7) by intramolecular dehydration[7] (e.g., with acid anhydrides, acid chlorides, DCC, heating etc.).



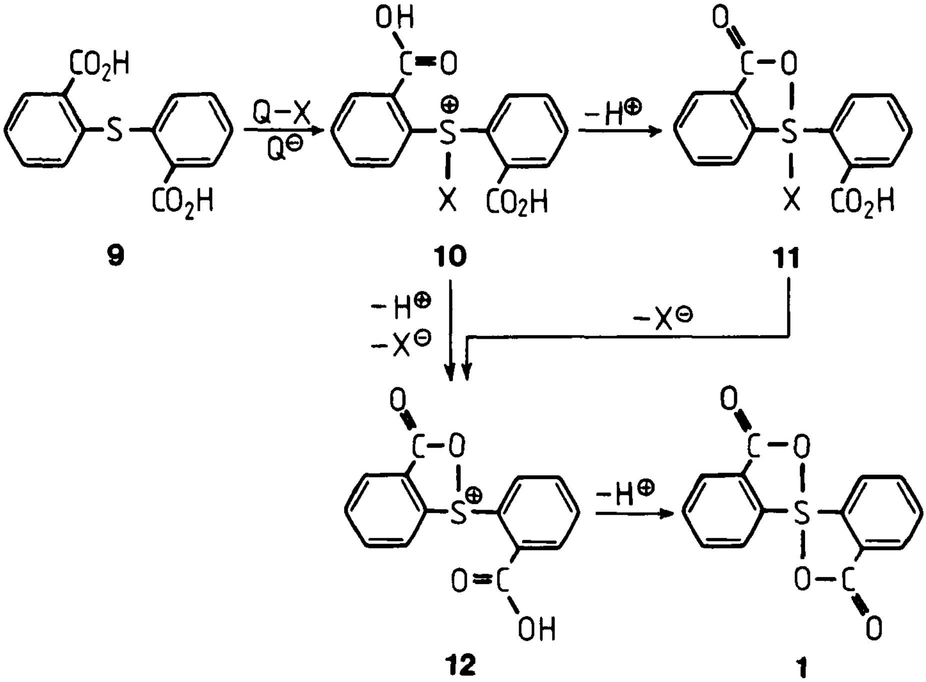
where Z = CH_2, C=O; Y = O, NCH_3

R^1, R^2, R^3 = H, NO_2, Cl, NHAc, OMe, $N(CH_3)$

Scheme 1

In our recent investigations[8] the corresponding starting sulfides (6) and sulfoxides (7) were substituted by hydroxymethyl, carboxyl and carbamoyl functional groups at *ortho* positions and with electron-withdrawing or electron-donating groups at *ortho* and/or *para* positions. Spirosulfuranes with six- or seven-membered rings were prepared by applying sulfides which contained 1,8-substituted naphthalene or 1,1'-substituted diphenyl moieties instead of the benzene rings.

The mechanism for the formation of spirosulfuranes from sulfides with halogenating agents was suggested by us.[6] In *Scheme 2* the *o,o'*-diphenyl sulfide (9) is used as a model. The existence of the reactive intermediate chlorosulfonium ion 10 has been evidenced by kinetic measurements reported by Ruff and Kucsman.[9a-d] Due to the intramolecular attack of one of the *ortho* carboxyl groups, the cycloacyloxy sulfonium salt 12 may be directly formed from the sulfonium salt 10 or through monocyclic chlorosulfurane intermediate 11. In the last



where Q = TsNH, TsNCl, *t*-BuO, Cl, $(CH_2CO)_2N$;
X = Cl, Br

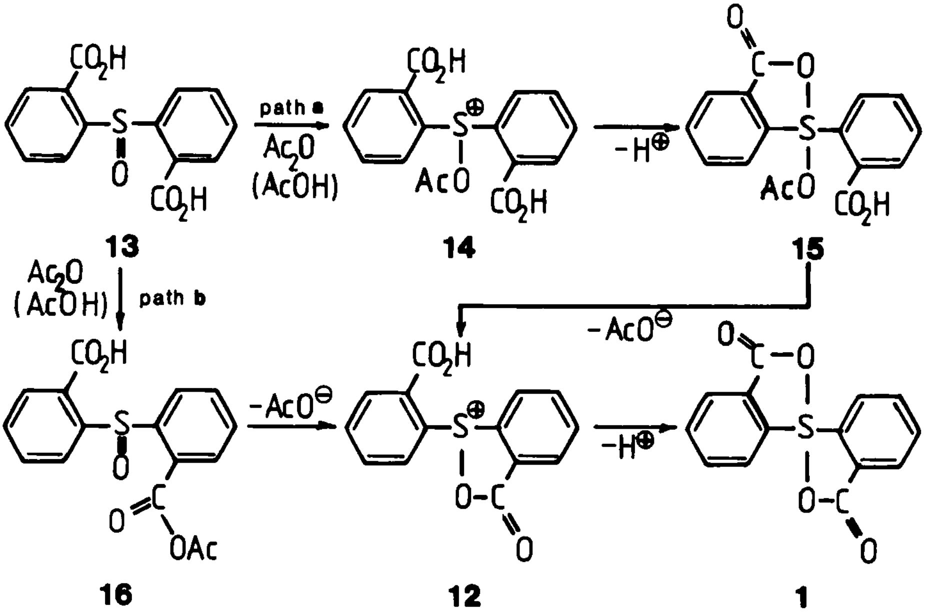
Scheme 2

stage the intermediate **12** is stabilized by the nucleophilic addition of the second *ortho* carboxyl group.

It should be pointed out that the structures of intermediates **10** and **12** clearly show that in these cases the structural conditions are very favourable for 1,5-type sulfur-oxygen close contacts. These structural conditions have been determined by Kucsman and coworkers on the basis of experimental data and of theoretical calculations with the conclusion that the strongest $S\cdots O$ close contacts may be regarded as "premature" hypervalent bonds similar to those found in certain nonsymmetric dioxysulfurane derivatives.[10a,b] These conditions are present for **10** and **12**, because there are possibilities for a planar 5-membered ring in a conjugated $X-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$ part (X = Cl, O), for a nearly linear $X-S^{\oplus}\cdots O=$ arrangement with an $X-S^{\oplus}\cdots O=$ angle of 169-173°, for an $S^{\oplus}\cdots O=$ interatomic atomic distance <3.25 Å, and because the "counter atom" X is electronegative and polarizable.

The mechanisms for the intramolecular dehydration of spirosulfurane precursor sulfoxides were determined by means of ^{18}O-tracer technique and reported by us[7] in 1979. The run of these type of reactions is demonstrated on *Scheme 3* using *o,o'*-dicarboxydiphenyl sulfoxide (**13**) as a model and with dehydrating agent acidic anhydride.

In the course of the dehydration three main steps can be distinguished: a) activation of the functional groups in the reaction **13** ⟶ **14** resulting in an acyloxysulfonium salt (**14**, *path a*) and/or in the reaction **13**⟶**16** by the formation of a mixed anhydride type of compound (**16**, *path b*); b) formation of a monocyclic sulfonium ion (**12**, identical to those found



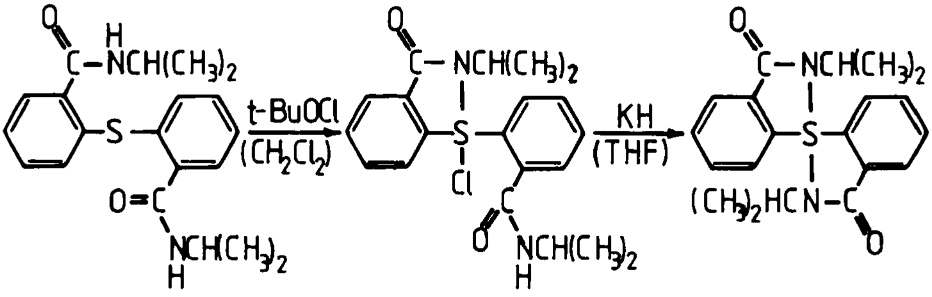
Scheme 3

in spirosulfurane formation with halogenating agents); c) nucleophilic addition of the remaining functional group leading to the end product spirosulfurane (1) involving a proton-transfer or a proton loss promoted by a base.

Isolated Intermediates in Spirosulfurane Formations from Sulfides with Halogenating Agents

Our studies centered on the preparation of intermediates involved in spirosulfurane formations, with the object of determining their molecular structures to explore correlations between structure and chemical properties.

The application of the reaction for spirosulfurane formation reported by Martin and coworkers[11] was suitable to reach our goal (*Scheme 4*).



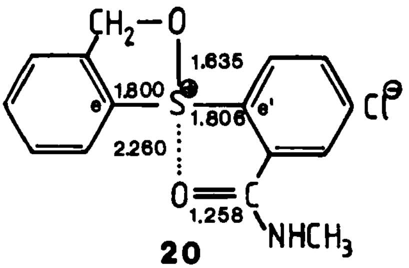
17 **18** **19**

Scheme 4

The spirosulfurane 19 was synthesized from the corresponding sulfide 17 with the isolation of the intermediate 18. They used *t*-BuOCl as chlorinating agent, and the structure of the intermediate 18 was assigned as chloroazasulfurane.[11] The intermediate 18 could be transformed into the spirosulfurane 19 only with potassium hydride.

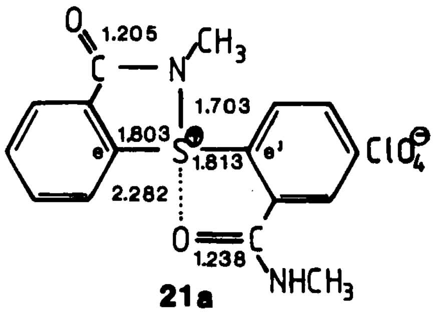
In a similar fashion, we prepared spirosulfurane precursors 20, 21a and 21b and determined their molecular structures.[12] It is interesting to note that these spirosulfurane precursors and the spirosulfuranes prepared from them hydrolyze in aqueous solutions into the corresponding sulfoxides.

The molecular structures of these models exhibit a sulfonium salt- and no chlorosulfurane character (cf. Ref. 12). The arrangements of the ligands about the sulfonium center can be described with a slightly



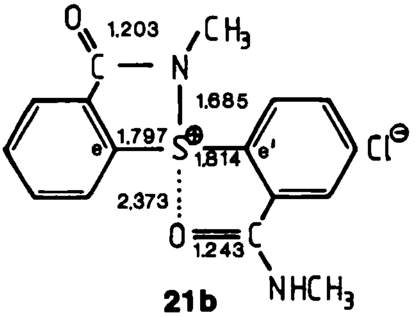
20

O—S···O	179.4,
C_e—S···C'_e	101.9,
C_e—S···Cl	166.5°
S···Cl	3.370Å



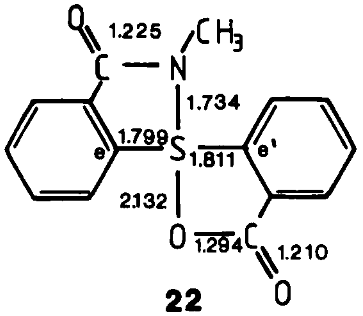
21a

N—S···O	179.0,
C_e—S—C'_e	101.8,
O(O_3Cl)···S—C_e	177.6°
S···O(O_3Cl)	2.886Å



21b

N—S···O	178.3,
C_e—S—C'_e	101.2,
C_e—S···Cl	173.9°
S···Cl	3.382Å



22

N—S—O	178.9,
C_e—S—C'_e	104.1°

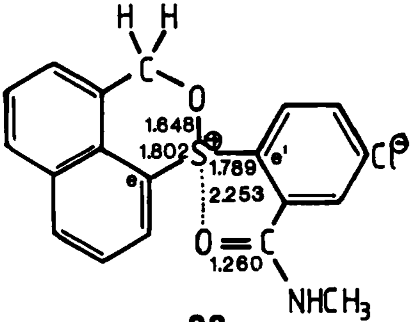
distorted TBP geometry (disregarding the anions). In axial directions the nearly linear O-$S^{\oplus}$···O= or N-$S^{\oplus}$···O= arrays suggest the existence of a three-center four-electron (hypervalent) bond system which may form by a very strong $S^{\oplus}$···O(carbonyl) through space interaction (cf. Refs. 5a-c and 10a,b). The anions being practically in the equatorial plane, approach the sulfonium center asymmetrically as described by Britton and Dunitz[13] for the nucleophilic attack on sulfonium ion. The interaction between sulfur and chloride is practically ionic (sum of van der Waals radii,[14] 3.59 Å). When chloride is replaced by perchlorate, some contact can be observed between the sulfonium center and the perchlorate oxygenes (sum of van der Waals radii[15] for oxygen and sulfur 3.25 Å).

To make a comparison between the suggested $N-S^{\oplus}\cdots O=$ hypervalent bond system and the analogous N-S-O bond system to be found in sulfuranes, we prepared[16] spirosulfurane **22** and determined its molecular structure[17]. The data presented show that although there are some deviations in S-N bond lengths and $C_e-S-C'_e$ bond angles, the basic arrangement of the ligands is the same.

Bearing the above structural data in mind with especial regard to the arrangement of the ligands, one may ask: why do we not regard these intermediates as sulfuranium salts? Mainly, because we can't observe any $O-S^{\oplus}$ or $N-S^{\oplus}$ bond elongation in the $O/N-S^{\oplus}\cdots O=$ arrays of these species, and even the determined data are somewhat shorter than the sum of covalent radii[3] (for O-S it is 1.70 and for S-N 1.74 Å). Another point to note is that the S(IV)[C,C,O/N] moieties exhibit a pyramidal configuration with bond lengths and bond angles similar to those found in analogous sulfonium salts[18a-c] as well as in sulfoxides[18d-g] and sulfilimines.[18h,j]

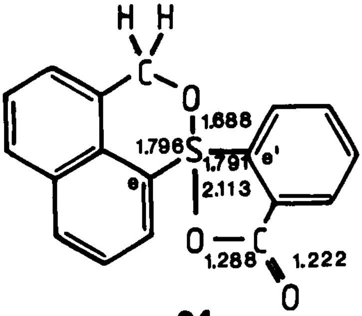
To gain further insight in this topic, we prepared cyclic sulfonium salts **23**, **25** and **27** and analogous spirosulfuranes **24** and **26** with six-membered rings and determined their molecular structures to compare the structural data about sulfur.[17,19]

Of the results of these investigations the most significant finding is that, while in cases of



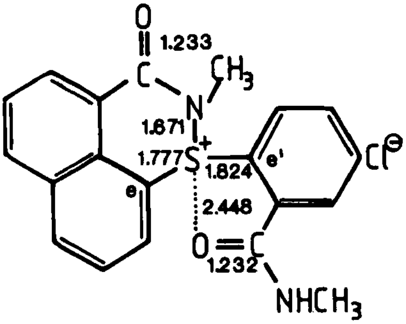
23

O—S·····O 173.9,
C_e—S—C'_e 104.7°
S·····Cl 4.272 Å



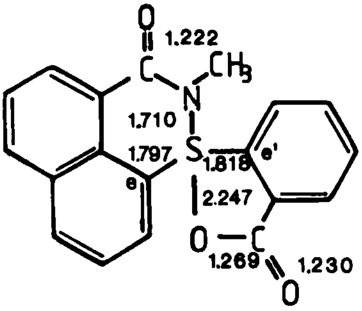
24

O—S—O 178.3,
C_e—S—C'_e 106.3°



25

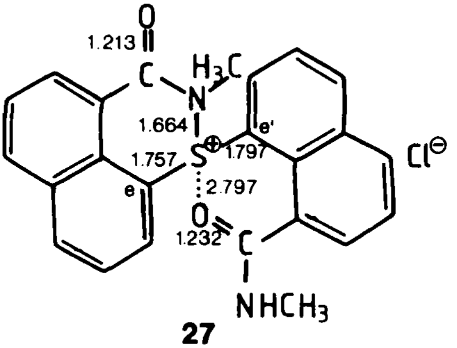
N—S·····O 164.9,
C_e—S—C'_e 101.4,
C'_e—S·····Cl 173.6°
S·····Cl 3.181 Å



26

N—S—O 174.2,
C_e—S—C'_e 105.6°

analogous spirosulfuranes 24 and 26 there are practically no changes in geometric parameters about sulfur in comparison to spirosulfuranes having five-membered rings, the arrangement of the ligands in the series of cyclosulfonium salts with six-membered rings (23, 25 and 27) can only be described with a considerably distorted TBP geometry. In these latter cases the axial angles range from 174^{o} to 157^{o}, and the interatomic distances between chloride anion and sulfonium center are beyond the sum of van der Waals radii[14] (3.59 Å) except in the case of cyclic sulfonium chloride 25.

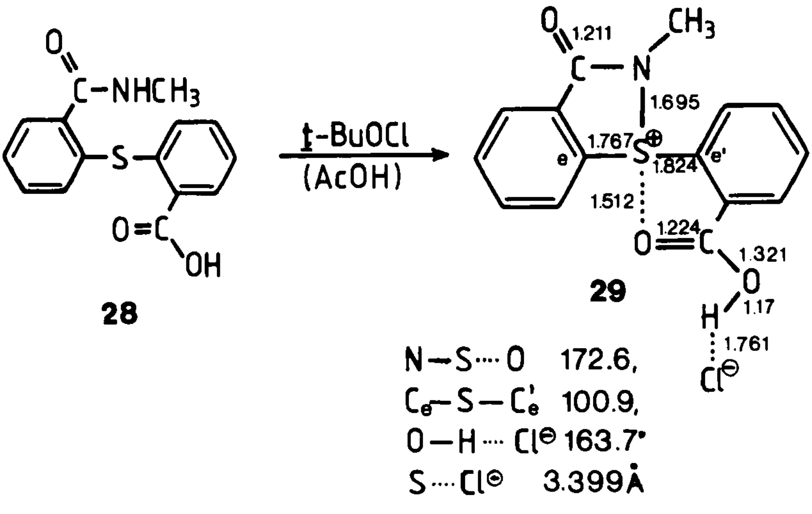


27

$N-S\cdots O$ 156.6,
C_e-S-C_e' 105.3°
$S\cdots Cl$ <5.74>Å

The cyclic sulfonium salt 27 possesses two six-membered spirorings with $S^{\oplus}\cdots O=$ interaction. The value for the axial angle is only 156.6^{o}, and the $S^{\oplus}\cdots O=$ interatomic distance is considerably longer than the other ones found for such type of sulfonium salts. The relatively long $S^{\oplus}\cdots O=$ interatomic distance is in accordance with the observations and calculations of Kucsman and coworkers, and can be considered as a "six-membered ring effect" (cf. refs. 10a,b). It is also remarkable to note that the cyclic sulfonium salt 27 could not be transformed into the corresponding spirosulfurane and could not be hydrolized into sulfoxide under the circumstances we used for the other cyclic sulfonium salts investigated by us[19]. The reasons for these discrepancies are under investigation.

The cyclic sulfonium salt **29** can be regarded as an intermediate in the last stage of spirosulfurane formation with halogenating agents (see *Scheme 2*, nucleophilic addition of the remaining carboxyl group on the sulfonium center). We were able to get to the crystals of this very interesting species by treating the sulfide **28** with *t*-BuOCl in acetic acid solvent at room temperature.[17] The intermediate **29** is stable at room temperature, but on contacting water it immediately transforms into the corresponding spirosulfurane **22**. It was also observed that *in vacuo* the crystals of **29** lose their hydrogen chloride resulting in spirosulfurane **22** (e.g., when kept in exsiccator *in vacuo* for a night.

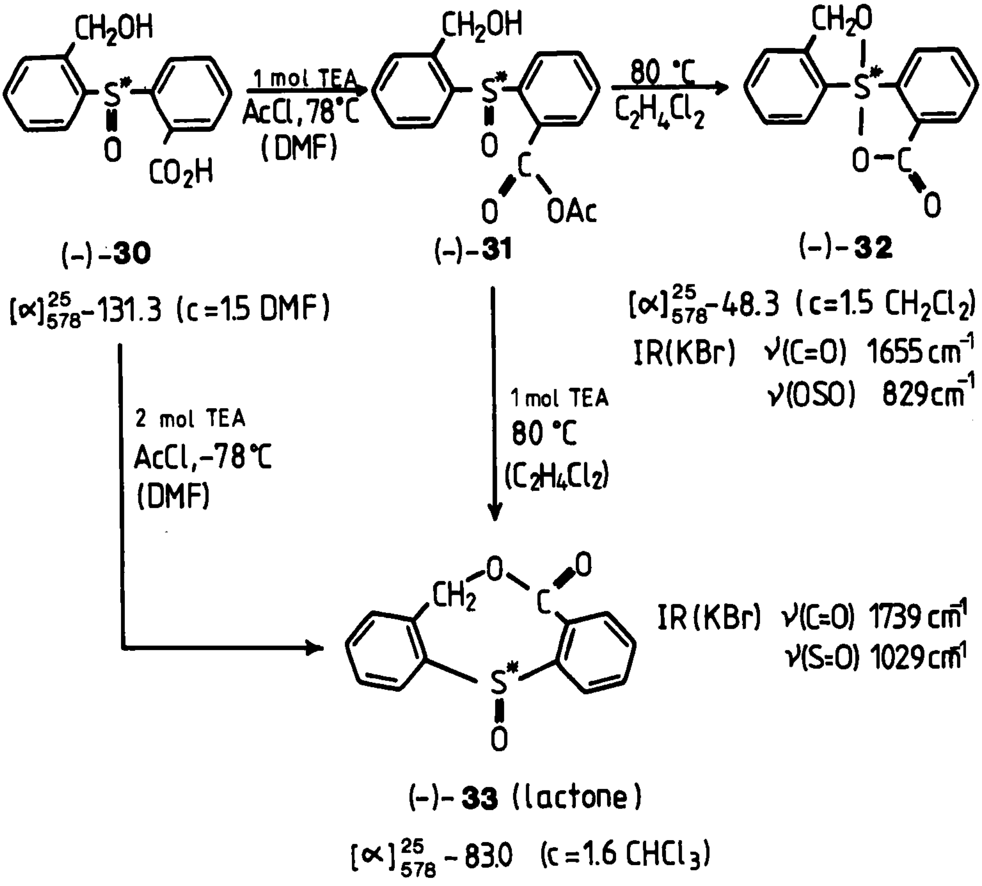


The molecular structure determination by X-ray methods[17] shows the chloride in hydrogen bonding with the hydrogen of the carboxylic hydroxy (sum of covalent radii[3] for hydrogen and chloride 1.27 Å).

Isolated Intermediates in Spirosulfurane Formations from Sulfoxides by Intramolecular Dehydrations

We are interested in the investigations of the stereochemical properties of spirosulfuranes, in order to clear up the mechanisms of some reactions which involve sulfuranes as intermediates. To determine these properties we had to synthesize spirosulfuranes in optically active form. For this reason we studied the mechanisms of both of the spirosulfurane syntheses. The experiments starting from optically active sulfoxides met with success.[20] In the following, two successful procedures leading to optically active spirosulfuranes will be demonstrated where the intermediates of the first step of spirosulfurane formation were isolated.

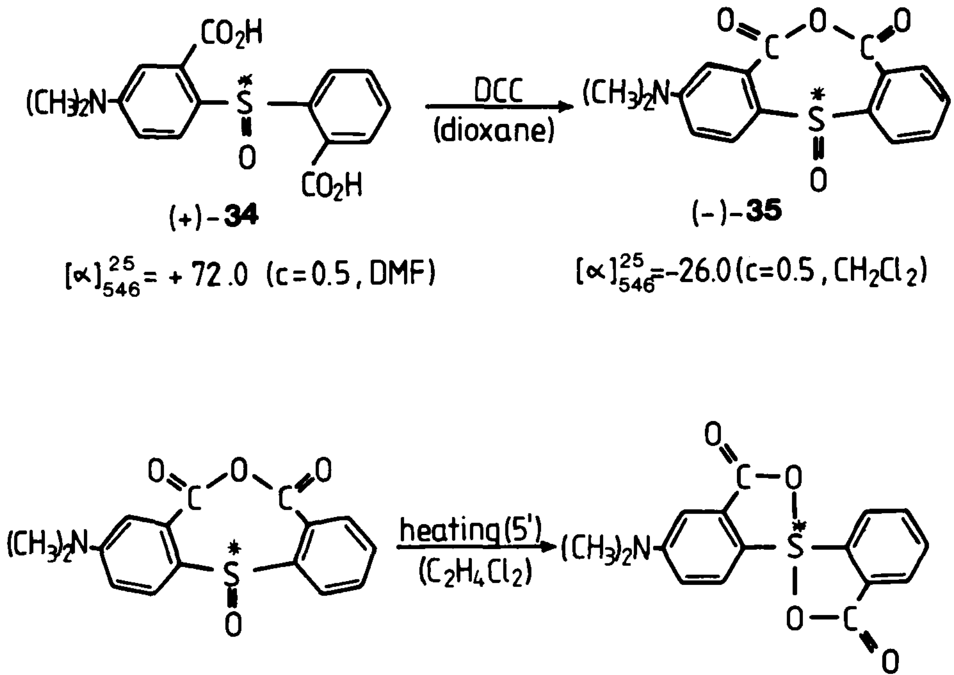
The intramolecular dehydration of the optically active sulfoxide **30** may result in the formation of spirosulfurane **32** and/or "sulfoxide-lactone" **33** in optically active form[8,20] *(Scheme 5)*. After a wrong assignation of the structure of one of the possible reaction products (lactone **33** had been assigned as spirosulfurane **32**)[21], we realized that using AcCl-TEA dehydrating system, the ratio of the spirosulfurane **32** to the lactone **33** depends on the amount of triethylamine (TEA) in the reaction mixture. When the TEA is used only in one molar equivalent amount to the sulfoxide **30**, we can get to the desired optically active spirosulfurane **32** by heating of the isolable intermediate **31** of mixed anhydride type in tetrachloroethane for some minutes.



Scheme 5

However, using TEA in two molar equivalent amount, the dehydration process resulted in the lactone 34 with eight-membered ring. The existence of intermediate 31 in both reactions has been proved by the reaction 31 → 33.

The diaryldiacyloxy type of spirosulfurane 36 was also prepared in optically active form *(Scheme 6)*



(+)-**34** $[\alpha]_{546}^{25} = +72.0$ (c=0.5, DMF)

(-)-**35** $[\alpha]_{546}^{25} = -26.0$ (c=0.5, CH_2Cl_2)

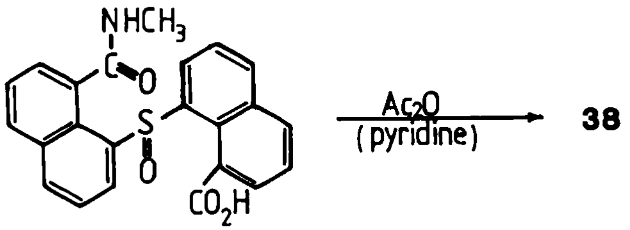
(-)-**35**
IR (KBr) ν(C=O) 1792, 1725 cm^{-1}
ν(S=O) 1019 cm^{-1}

(-)-**36** $[\alpha]_{546}^{25} = -29.3$ (c=0.5, DMF)
Ep ≅ 60%

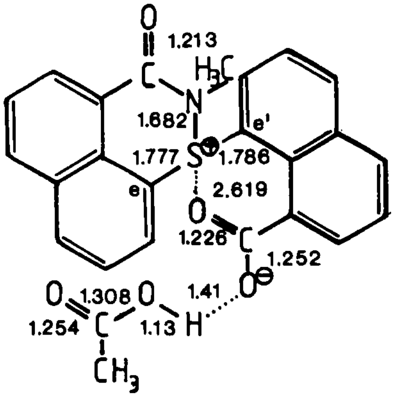
Scheme 6

starting from the optically active sulfoxide 34, followed by a brief heating of the isolated intermediate 35.[8,20] In this preparation DCC was used as a suitable dehydrating agent for the formation of the cyclic anhydride 35 with eight-membered ring.

The cyclic sulfonium salt type of intermediate **38** is a model characteristic of the last step of spirosulfurane formation from sulfoxides by intramolecular dehydration[19] (see *Scheme 3*). The intermediate **38** can be isolated directly from the reaction mixture when sulfide **37** is dehydrated with acetic anhydride in pyridine resulting in this species as a hydrogen bonded molecular complex with one mol equivalent acetic acid. It can also be regarded as the first isolated intermediate in the proton-transfer process of spirosulfurane formation starting from 2-carboxyaryl sulfoxides. The hydrogen bonding is relatively strong, in comparison: in ice the H···O interatomic distance[22] is 1.79 Å.



37



38

O—H·····O⊖	2.51 Å
N—S·····O	159.0,
C_e—S—C'_e	103.5,
O—H·····O⊖	161.7°

ACKNOWLEDGEMENT

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