ORGANIC SULFITES

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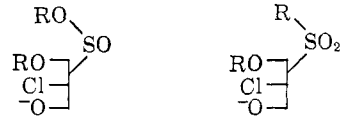
I. INTRODUCTION

A. DEFINITION AND NOMENCLATURE

Organic sulfites can formally be derived from sulfurous acid with the hypothetical structure $(HO)_2S{=}O$, by a double esterification with an alcohol function. In practice they are most commonly synthesized with thionyl chloride, which can be regarded as an acid chloride of sulfurous acid. These esters (Eng.: "sulphites"; F.: "ethers sulfureux," "sulfite neutre"; G.: "schwefligsäure Ester"; sometimes: "thionyl" compounds) are therefore characterized by a sulfite group, SO_3, linked to an organic skeleton by two C–O bonds. A distinction may be made between symmetrical compounds in which two similar radicals are linked to this group, asymmetrical or mixed sulfites in which the radicals are different, and cyclic sulfites containing the sulfite group in a heterocyclic ring. For the latter a nomenclature may be adopted accordingly, reading, *e.g.*, for a five- or six-membered saturated ring: 1,3,2-dioxathiolane 2-oxide or 1,3,2-dioxathiane 2-oxide, respectively (IUPAC rules 1957).

B. HISTORICAL

This class of compounds has been known since 1846 and has repeatedly been object of investigation for reasons of theoretical interest, arising from their chemical reactivity and their structural features, as well as for practical purposes, *e.g.*, application as insecticide. Apart from this, numerous sulfites appear to have been obtained in the course of other directed investigations, such as attempts to synthesize a chloride from an alcohol using thionyl chloride and have been communicated in the literature as such without detailed examination. The circumstance that sulfites are isomeric with sulfonic esters has caused occasional confusion in the earlier literature, particularly as regards the acid



chlorides (38, 87) and metal salts (199, 237, 240) of the two respective classes. As sulfonic esters and ionic sulfonates are derivable from inorganic metal sulfites, these compounds were originally denoted as "sulfurous" in the German literature. The name sulfite may still be encountered for the "sulfonic" addition products of olefins with bisulfite.

C. SCOPE OF REVIEW

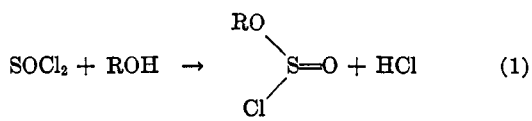
Up to the present moment a survey of the literature of organic sulfites is lacking, while the well known

handbooks on the chemistry of organic sulfur compounds contain very little if any information about this class of compounds. This prompted the author to write the present survey. It reviews the literature up to mid-1962 and includes in the list of references all publications of which the author is aware. A restriction is made, however, with respect to publications dealing with sulfites only casually, for example, only in connection with the replacement of hydroxyl groups by chlorine *via* chlorosulfinates, or in connection with the physicochemical properties of compounds of related structure. Numerous and often difficult to trace are places where (new) sulfites are mentioned briefly, apparently without having been investigated any further. All these publications as well as the patent literature are covered only to a limited extent. Metal alkyl sulfites and chlorosulfinates are discussed where relevant to the chemistry of sulfite esters.

II. Preparation

A. General Methods

In the oldest method of preparation (27, 35, 36, 37, 68) aliphatic sulfites were obtained among other products, such as alkyl chlorides and mercaptans, from a reaction between sulfur monochloride and alcohols. The reaction requires an excess of alcohol and gives low yields only. Carius (35, 38) presuming thionyl chloride to be produced in this reaction as the actual cause of the formation of sulfite, investigated the direct action of it on alcohols and by doing so found a much better method of synthesizing organic sulfites. These compounds have since been prepared almost exclusively in this way. Under suitable conditions, notably in the presence of a catalyst (*vide infra*), thionyl chloride reacts readily with most alcohol functions to give a sulfite in high yield. The reaction involves the intermediate formation of a chlorosulfinate.



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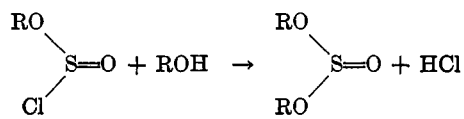

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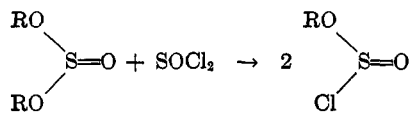
side reactions:



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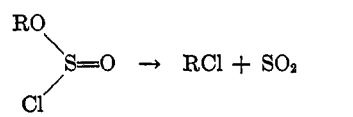


(4)

The synthesis is easily achieved by the gradual addition of thionyl chloride to a primary or secondary alcohol in the proportions 1:2 (11). The reaction mixture is usually cooled and stirred (139, 217, 230). This may also be effected by the passage of an inert gas such as carbon dioxide (234, 236), which carries away the generated hydrogen chloride. After completion of the addition of thionyl chloride the mixture is often refluxed for some time or heated on a water bath until hydrogen chloride is no longer evolved. Many cyclic sulfites from aliphatic, in some cases aromatic, diols and polyhydric alcohols have been prepared in essentially the same way, sometimes with heat applied at the start of the reaction (55, 244). The use of a suitable solvent, such as carbon tetrachloride, chloroform, ether, or petroleum ether may be profitable, particularly if the end product is a solid (72, 128). It offers the advantage that hydrogen chloride is smoothly removed and enables purifications to be carried out (extractions with dilute base, water) prior to distillation.

In a slightly modified version, known as "refluxing solvent technique" (21, 170), the reactants are added simultaneously in the required proportions to a solvent of suitable boiling point in which hydrogen chloride is insoluble. Reactions 1 and 2 have been studied in this way under a variety of conditions and were found to be much faster than reaction 3. This might also be concluded from the fact that numerous sulfites have been prepared successfully with the use of an excess of thionyl chloride; *e.g.*, the sulfites of *d*- or *l*-*sec*-octanol (118, 140), fenchyl alcohol (202), phenol (22) and the cyclic sulfites of ethylene or trimethylene glycol (148), pentaerythritol (101), catechol (1), alizarin (102), and some other dihydroxy derivatives of anthracene (103). That reaction 3 can be very slow for cyclic compounds is evident particularly with diols from which cyclic sulfites were isolated as main product in obvious attempts to replace the hydroxyl groups by chlorine: *l*-2,3-butanediol (197); 2-amino-3-methylpropane-1,3-diol (125); 2,2-diphenylpropane-1,3-diol (153); pentaerythritol (100); *cf.* also the cyclic sulfites obtained in the preparation of nitrogen mustards (127, 201).

Another procedure, applied only for diphenyl sulfite, consists in reacting thionyl chloride with a suspension of sodium phenolate in toluene or ether (13, 236). But the yields were definitely lower than with the refluxing solvent technique, which gives 85% within 2 hr. at 130° in chlorobenzene (22).

Darzens' discovery that the replacement of a hydroxyl group by a chlorine atom with thionyl chloride is greatly facilitated by using a tertiary nitrogen base (61) provided a valuable new means for preparing sulfites. It appears that with tertiary bases, such as pyridine, quinoline, or triethylamine, reaction 2 is strikingly enhanced, and sulfite formation becomes a quite general and quantitative reaction which will take place readily, even at temperatures as low as −78°. As the base catalyst is blocked by hydrogen chloride

during the reaction, it must be added in stoichiometric quantities. The most common procedure is the dropwise addition of the theoretical amount of thionyl chloride to a solution of hydroxy compound and pyridine in ether or benzene with stirring. When this reaction is carried out at room temperature or slightly lower, a fine precipitate of the pyridine salt, which can be easily filtered, results. Extracting of the filtrate with dilute hydrochloric acid and bicarbonate solutions has the advantage that most impurities are removed, and after subsequent drying and evaporation of the solvent, a rather pure product in excellent yield is usually obtained. The symmetrical sulfites of a number of substituted alcohols (96) and phenols (121, 185, 205) have been prepared in this way; similarly for olefinic alcohols (79), aliphatic hydroxy esters (93), and, for example, 1,1,1,3,3,3-hexachloro-2-propanol which shows no reaction with plain thionyl chloride (92); also cyclic sulfites of 1,2- and 1,3-glycols (29, 167) and some aromatic diols (103, 104, 105, 106).

The synthesis of an asymmetrical sulfite is effected by starting from a chlorosulfinate *via* reaction 2. The use of an equivalent amount of base is necessary to prevent the product from disproportionating into two symmetrical compounds (40, 236). Here again it is common practice to employ a solvent in which the base hydrochloride will precipitate. Numerous mixed sulfites with aliphatic as well as aromatic radicals have been reported (42, 43, 110); for compounds containing a methyl radical (see 19, 25, 76).

An extensive study of the reactions 1 to 4, particularly concerned with influence of pyridine thereon, has been made by Gerrard (88, 89, 90, 91) with other investigators (79, 80, 81, 95, 96). Earlier observations were by Carré, Mauclère, and Libermann (40, 41, 43, 44, 46, 49). The following findings pertain to the synthesis of sulfites and chlorosulfinates:

(*a*) The reaction between thionyl chloride and alcohol may yield a chlorosulfinate directly if the alcohol is added to a slight excess of thionyl chloride. If the order of mixing is reversed, a sulfite is formed as well; the sulfite takes much longer time at room temperature to react further with thionyl chloride. For the latter reaction (reaction 3) pyridine hydrochloride is a powerful catalyst.

(*b*) Thermal decomposition *via* reaction 4 is facilitated by pyridine hydrochloride as well, even to such an extent that primary chlorosulfinates cannot be isolated from a reaction mixture in the presence of this catalyst while secondary chlorosulfinates change to alkyl chlorides and olefins even under the mildest conditions.

(*c*) Chlorosulfinates react vigorously with free pyridine at room temperature or even below, by two distinct mechanisms leading to alkyl pyridinium chlorides and alkyl chlorides, respectively.

(*d*) Tertiary bases therefore are to be avoided in the preparation of chlorosulfinates. The latter may then be distilled under reduced pressure so far as their poor stability permits; *e.g.*, the lower homologs of primary alkyl chlorosulfinates (88), chloroalkyl chlorosulfinates (110, 131), chlorosulfinates derived from secondary hydroxy esters (93), remarkably stable neopentyl chlorosulfinate (94), phenyl chlorosulfinate (90).

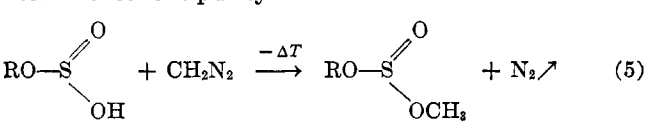
(*e*) Primary and secondary alcohols with an aromatic nucleus in α-position (phenyl carbinols) give a chloride rapidly even in the absence of catalysts. For these compounds it still has to be shown that chlorination, according to Darzens' procedure, goes *via* chlorosulfinates. The only evidence for their transitory existence is the fact that the corresponding sulfites can be made (96), even though this requires temperatures of $-10°$ or in some cases $-78°$.

(*f*) Sulfites derived from tertiary aliphatic alcohols are not known. Mixed sulfites containing one *t*-butyl group have been made, however, from a stable chlorosulfinate and subsequent reaction with the tertiary alcohol.

B. SPECIAL METHODS

A preparative method which has been used in a few cases only, but might be applicable more widely and must be considered as rather "clean," is based on a transesterification between dimethyl sulfite and the parent alcohol of the required sulfite. The cyclic derivatives of erythrol (20) and 1,4-dihydroxy-2-butene (187) have been obtained in high yields. The method was successfully applied for preparing dicyclohexyl sulfite (222), which was otherwise not always easily secured (50, 51, 134, 238). In the patent literature preparations of cyclic sulfites have been described from 1,2-epoxides by a reaction with sulfur dioxide (71, 198). The action of sulfur monochloride or thionyl chloride on these epoxides leads to β-chlorinated symmetrical sulfites (149, 171). Diethyl sulfite can be prepared from ethylene, water, and sulfur dioxide with silver sulfate as catalyst (181). Meuwsen (158, 159, 160) obtained this compound by oxidating diethyl sulfoxylate.

A remarkable synthetic procedure, reported only very recently (116, 172), starts from aliphatic diazo compounds. Alcoholic solutions of sulfur dioxide added to, *e.g.*, diazomethane, yield readily asymmetrical sulfites of excellent purity.



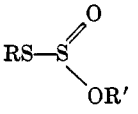
(5)

Organic selenites can be prepared in the same way (see the interesting article on selenites by Simon and Paetzold (210), who isolated, for example, a free alkyl selenous acid, $ROSeO_2H$, by crystallization).

C. SYNTHESIS OF COMPOUNDS CLOSELY RELATED TO SULFITES

By the action of sulfur monochloride or thionyl chloride on metallic salts of carboxylic acids (212) unstable "anhydrosulfites," $(RCO_2)_2SO$, may result. Somewhat similar to these are the cyclic sulfites obtained from α-hydroxyisobutyric acid and lactic acid (24).

A number of compounds described as esters of thiosulfurous acid or O,S-dialkyl thiosulfites



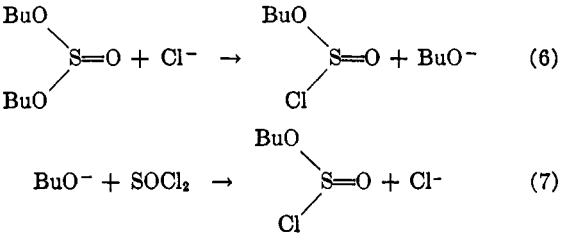
have been prepared from chlorosulfinates and mercaptans in the presence of pyridine (246, 247). The only compounds which might be called dithiosulfites have been obtained from 4-bromodithiocatechol and alkyl xanthogenic acids, respectively, by treating the corresponding potassium salts with thionyl chloride (107, 184).

A few sulfurous acid esters of hydroxylamines have also been reported (245). They differ from sulfites in that one radical is replaced by a substituted nitrogen center.

III. Chemical Properties

A. INTERACTION WITH THIONYL HALIDES AND HYDROGEN HALIDES

The replacement of a hydroxyl group by chlorine by means of thionyl chloride involves the intermediate formation of a chlorosulfinate, which by a process of internal substitution (SNi) goes to a chloride with retention of configuration. Occasionally in such reactions a high percentage of sulfite is produced (57). The reaction proceeds under milder conditions if Darzens' procedure is applied, *i.e.*, if an equimolecular quantity of pyridine is added, but in this case the interaction with thionyl chloride leads to a chloride of predominantly inverted configuration. The explanation is that chloride ions originating from the produced pyridine hydrochloride will now participate in the substitution (10, 90). In this procedure a sulfite is formed in a first stage and the "smoothness" of the reaction is caused by the pyridine salt which plays a catalytic role both in the conversion of sulfite into chlorosulfinate and in the decomposition of the latter (compare reactions 3 and 4 in the previous section). In fact catalytic amounts of pyridine hydrochloride are sufficient to bring about a reaction between, *e.g.*, pentaerythrityl disulfite and thionyl chloride (101) which might otherwise fail completely. The reaction is similar with thionyl bromide and has been reported as a general method for preparing alkyl bromides from dialkyl sulfites (80). Bartlett and Herbrandson (12) have investigated kinetically the reaction between dibutyl sulfite and thionyl chloride in nitrobenzene as solvent and in the presence of benzyl pyridinium chloride. Their findings are consistent with the following ionic chain mechanism.



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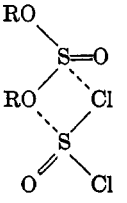
(7)

Herbrandson, Dickerson, and Weinstein (113) have shown that sulfinic esters react in a similar way. If thionyl chloride is allowed to react with sulfites in the absence of catalysts at room temperature over a considerable period of time (say 48 hr.), it may give a high yield of chlorosulfinate (213). It has been stated to be a convenient method for preparing compounds less accessible by the direct way, such as benzyl chlorosulfinate (46). Gerrard (89) has depicted this reaction as a "four center" approach.



However, the catalytic power of chloride ions appears to be so strong that traces will bring about conversion without this bimolecular reaction being of any significance. The sulfite of ethyl lactate gives a chlorosulfinate without configurational change at the adjacent carbon atom (77). With thionyl bromide, bromosulfinates are likewise formed (47).

Libermann (142, 143) has found that asymmetrical sulfites derived from primary alcohols, after saturation with hydrogen chloride and subsequent distillation, show disproportionation into two symmetrical sulfites. If one group consists of a benzyl or allyl radical, benzyl chloride and allyl chloride are produced, respectively. Bissinger and Kung (21), refluxing symmetrical sulfites of *n*-propyl and isopropyl alcohols with hydrogen chloride, also obtained chlorides, but the corresponding chlorosulfinates, if treated in the same manner, give a lower product yield. So it remains doubtful whether a chlorosulfinate occurs as intermediate in this reaction. Yet, the cleavage of the cyclic sulfites of hydrobenzoin and isohydrobenzoin by heating with hydrogen chloride in dioxane resulted in chlorohydrins in which the initial configuration was retained (183).

The action of hydrogen iodide on diethyl sulfite in benzene–carbon tetrachloride solution, according to

$$(C_2H_5O)_2SO + 6HI \rightarrow 2C_2H_5OH + H_2S + H_2O + 6I \quad (8)$$

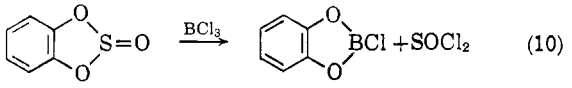
proceeds *via* the formation of thionyl iodide (227).

B. SULFITES AS ALKOXYLATING AGENTS

The reaction with thionyl chloride, mentioned previously, shows the capability of sulfites to transfer an alkoxyl group in exchange for chlorine. This alkoxylating property displayed by sulfites in reactions with several inorganic chlorides and acid chlorides can be summarized in the equation

$$(RO)_2SO + ACl_n \rightarrow ROSOCl + ROACl_{n-1} \quad (9)$$

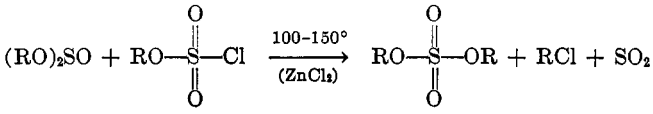
Depending on the reaction conditions involved, the formed chlorosulfinate may decompose. Thus, with boron trichloride a chlorosulfinate is produced and a boron compound in which up to three chlorine atoms are replaced by alkoxyl groups (53). For *o*-phenylene sulfite a similar behavior has been observed.



(10)

The reaction of sulfites with phosphorus pentachloride has given rise to some controversy in the earlier literature (40, 42, 97, 162). Carried out in the cold, however, it was found to be a convenient means for preparing chlorosulfinates with high yields (28, 131). Here phosphorus oxychloride and alkyl chloride are the other products. This is in accord with reaction 9 if an immediate decomposition of $ROPCl_4$ is assumed. The synthesis of aromatic chlorosulfinates is not practicable in this way; triaryl phosphates result instead (45).

With sulfuryl chloride chlorosulfonates are formed, which may continue at elevated temperatures to react with a second mole of sulfite to give dialkyl sulfates (137).



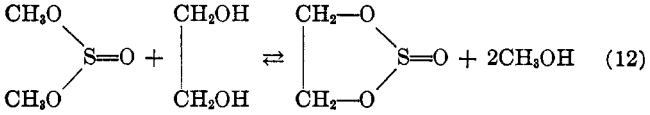
(11)

With other acid chlorides and anhydrides the formation of esters is quite analogous (66, 137, 139). Barkenbus and Owen (11) secured exceedingly pure higher homologs of primary dialkyl sulfates with yields of 50 to 80%, by starting from sulfuryl chloride and an alcohol and performing reaction 11 with the crude chlorosulfonate. Apart from alkyl chlorides they also found olefins and hydrogen chloride among the products.

When aliphatic sulfites are heated with carboxylic acids, alkyl esters are obtained in almost quantitative yield if some mineral acid is also added (236). It has been stated that the sulfite is only indirectly involved in this esterification by removing water from the reaction mixture (hydrolysis) and thus shifting the equilibrium in a favorable direction. A remarkable esterification procedure with aromatic sulfites was described more recently (121, 122, 205). Carboxylic acids can readily be esterified by adding electronegatively substituted diphenyl sulfites in the presence of a tertiary base. A smooth migration, presumably of phenoxide ions, takes place giving aryl esters at room temperature in high yields. The method has been used for synthesizing *p*-nitrophenyl esters of amino acids and polypeptides.

C. TRANSESTERIFICATION

Transesterifications without catalysts have been observed for aliphatic compounds after refluxing with alcohols different from those from which they are derived. This furnishes new sulfites. Dimethyl sulfite has been used in this way for preparative purposes (20, 187). The reaction is possibly a reversible alcoholysis which will proceed in one direction owing to a continuous removal of methanol from the reaction mixture. This is suggested by the fact that dimethyl sulfite and ethylene sulfite set up an equilibrium with their respective alcohols.



(12)

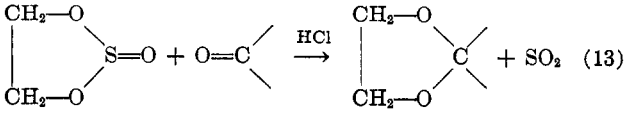
The equilibrium may be reached from either side after 20 months, the components being finally present in comparable amounts (63). In the series of dialkyl esters there seems to be a tendency for higher homologs to be formed from lower ones (28). It may be asked whether a synthesis of mixed sulfites could be accomplished in this manner. The circumstance, however, that mixed sulfites disproportionate easily into two symmetrical compounds in the presence of hydrogen chloride (142, 143), or during distillation (19, 43), indicates that they are less stable. It is also the reason why tertiary nitrogen bases are used in the synthesis of mixed sulfites from a chlorosulfinate and an alcohol. It is unlikely though that such an exchange occurs spontaneously with noticeably speed at ordinary temperatures (28) if all traces of acid are thoroughly removed.

Pyridine was found to promote a transesterification between bis-(*p*-nitrophenyl) sulfite and phenol (121).

D. ACETAL FORMATION

The preparation of acetals has been effected with aliphatic sulfites in the presence of mineral acid as catalyst. Especially for ketones and aromatic aldehydes as well as for preparing α- and β-methyl glucosides from sugars, this method was found advantageous (235).

Recently a synthesis of ethylene ketals was reported (115) in which ethylene sulfite was used with some hydrochloric acid.



(13)

The yields for benzaldehyde and a number of aliphatic ketones varied from 50 to 70%.

E. HYDROLYSIS

Under acidic and alkaline conditions, or even spontaneously in the presence of water, organic sulfites hydrolyze to the alcohol from which they are derived, with retention of configuration. The only exception to this rule reported (75) is that the alkaline hydrolysis of the cyclic sulfite of *cis*-1,2-cyclohexanediol yields almost exclusively *trans*-1,2-diol, contrary to the reaction in acid. In the earliest reported experiments on alkaline hydrolysis (2, 199) alkali salts of sulfonic acids were found among the products. Baggesgaard–Rasmussen (9), reinvestigating this point, concluded that hydrolysis is normal in excess base where the reaction is fast and complete, but under conditions where unreacted dialkyl sulfite and inorganic sulfite can interact slowly, a small percentage of alkane sulfonate may be formed, analogous to the reactions observed by Strecker and Mayer (*vide* section IIIF, alkylation). Retention of configuration after hydrolysis was reported for some steroid sulfites (144) and cyclic sulfites of *erythro*- and *threo*-2,3-diols of butane and pentane, and 3,4-hexanediols (55), all in acidic media; for cyclic sulfites of *trans*-1,2-cyclohexanediol (75) and *d*-(−)-2,3-butanediol (84, 197) in acid as well as base.

Reaction rates and mechanisms have been studied in a series of investigations by de la Mare, Bunton, Tillett, and others (30, 31, 32, 33, 34, 62, 151, 152, 220, 221). From hydrolyses carried out in isotopically enriched water it appeared that for open-chain as well as cyclic aliphatic sulfites reactions take place with sulfur–oxygen bond fission only. Analysis of kinetic observations established that acid hydrolysis is a multistage reaction; a fast pre-equilibrium proton transfer is followed by a rate-determining bimolecular step in which a solvent molecule or nucleophilic anion participate. The anion catalysis can lead to an apparent dependence on Hammett's acidity function. A comparison of rates shows that diethyl S > trimethylene S > ethylene S in similar acid solutions. The effect of alkyl substituents on the rate is small for five- and six-membered cyclic compounds. In alkali the order or reactivity is reversed. Here the mechanism is nucleophilic attack by hydroxyl ions on the sulfur atom and S–O bond fission, leading to a half-ester, which decomposes under liberation of sulfite ions as soon as it is formed. Earlier reports (106, 185) on the observed stability of some aromatic sulfites toward aqueous alkali are misleading and probably refer to low solubility in water. They react roughly 10^5 times faster than corresponding aliphatic compounds do. Added salts have only little effect on the alkali-catalyzed reaction, with the exception of *o*-phenylene sulfite which shows catalysis by bisulfite ions (autocatalysis). This compound exhibits also an exceptionally high neutral rate of hydrolysis at normal temperatures.

F. SULFITES AS ALKYLATING AGENTS

An interesting property shown by aliphatic sulfites is their alkylating action on compounds containing suitable nucleophilic groups. Dimethyl sulfite is a particularly powerful alkylating agent. In these reactions, which involve fission of a carbon–oxygen bond, sulfites are converted into alkyl sulfite ions. This property is analogous to that of dialkyl sulfates and sulfonic esters. On the other hand, sulfite esters as well as salts can be isomerized to sulfonic esters and ionic sulfonates by being alkylated. The various reaction paths which relate these compounds, and all involve an alkylation step, are presented schematically in Fig. 1.

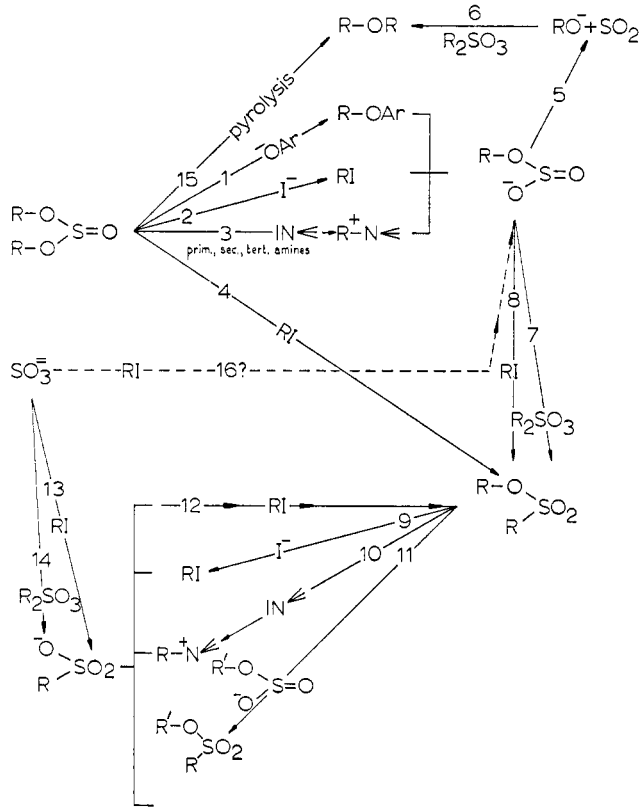


Fig. 1.—Possible reaction paths of alkylation.

O-Alkylation (route 1) occurs when sulfites are heated with sodium phenolates or alcoholates (52, 86, 123, 236). Aromatic methyl ethers and higher homologs up to isoamyl have been prepared in this way with high yields. Hydroxyethylation could be effected in some cases, using ethylene sulfite (39).

Alkylation of anions has also been realized with iodides and bromides (route 2). When cyclic sulfites of 1,3-glycols are refluxed in acetone with sodium iodide, sodium iodoalkyl sulfites are formed, easily hydrolyzable to the corresponding iodohydrins (147, 243). Foster, Hancock, Overend, and Robb (76) investigated the reaction for a number of dialkyl sulfites and methyl sulfites of carbohydrate derivatives, the latter yielding

methyl iodide exclusively. In boiling acetone as solvent the acetone bisulfite compound is also formed, though more slowly, due to decomposition of sodium alkyl sulfites by water arising from side reactions. Reaction at higher temperatures (120–150°) or prolonged interaction at room temperature leads to quantitative formation of sulfonates of the type $(RSO_3K)_4 \cdot KI$. The same double salts are formed directly from sulfonic esters with excess of potassium iodide (route 9). Potassium bromide reacts accordingly (200).

That it is indeed routes 8 and 9 which are followed, was suggested by Simon, Paetzold, and Kriegsmann (211). In a recent study on the mechanism of rearrangements with alkyl iodides and alkali iodides, these investigators re-examined for R = methyl under varied conditions the reactions reported in the older literature (2, 199, 200). It was established that both dimethyl sulfite and ionic methyl sulfite undergo alkylation on the sulfur atom by methyl iodide and yield methyl methanesulfonate (routes 4 and 8). At 155° the latter reaction seems to proceed more readily, but it continues *via* route 9 to give ionic sulfonate unless the iodide ions liberated in step 8 are blocked; silver methyl sulfite reacts spontaneously in the cold with methyl iodide to give the ester as final product.

Phenyl esters of alkanesulfonic acid do not seem to give reaction 9; they have been prepared from sodium phenyl sulfite *via* route 8 (203).

It may be mentioned that no rearrangements of this kind could be effected by the mere application of heat or light. Pure sulfite esters and salts remain unchanged on storage (132, 208).

The ease with which dialkyl sulfites have been transformed into sulfonates in the presence of aqueous alkali (3), suggests that it took place by a different process; it was undoubtedly due to hydrolysis of the sulfite followed by alkylation of inorganic sulfite. This reaction, route 13, is well known and named after Strecker (214).

$$RI + SO_3^{=} \xrightarrow[H_2O]{\Delta T} RSO_3^- + I^- \qquad (14)$$

Starting from silver sulfite, sulfonic esters result (133, 216) *via* routes 13–12 as the retrograde reaction 9 is now eliminated (211). Quite analogous to this is the alkylation of inorganic sulfite by dimethyl sulfate (154) or sodium ethyl sulfate (157) in hot aqueous solutions. It has been stated (9) that the formation of small amounts of sulfonate during slow saponification of sulfites with alkali, is presumably a similar reaction (route 14). The fact that Strecker's reaction is feasible under conditions where ionic alkyl sulfite cannot exist because of spontaneous hydrolysis, indicates that alkylation takes place on the sulfur directly and not *via* routes 16 and 8. This does not necessarily exclude, however, an alternative mechanism for nonaqueous media. It has been claimed, for example, that diethyl and dipropyl sulfite were obtained from silver sulfite and alkyl iodide (233). This would imply an alkylation on oxygen *via* route 16 and a reverted route 2. It should be noted that diethyl selenite was prepared similarly from silver selenite in excess of ethyl iodide (161).

Dimethyl sulfite and some higher homologs have been applied successfully for N-alkylating primary and secondary amines. Dimethylaniline was thus obtained in 96% yield (236), but attempts with diamyl sulfite and dimethylaniline did not result in alkylation (176). Isomerization of sulfites to sulfonic esters by catalytic amounts of tertiary amines is named after Bissinger (23). The mechanism, as proposed by Bartlett, is indicated by routes 3 and 7, with routes 5 and 6 as side reactions. It is seen that the actual catalyst of the reaction is the alkyl sulfite anion which is alkylated by aliphatic sulfite and simultaneously reformed.

The scheme may also serve to interpret observations by Voss and Blanke (236) who isolated hygroscopic salts from a reaction of dimethyl sulfite with pyridine or dimethylaniline at room temperature. Although the properties of these salts pointed without doubt to their structure as anilinium or pyridinium methyl sulfites, they seem not to have been recognized as such, as conversion into sulfonates was unsuccessful, but it is now obvious that after isolation of "pure" catalyst a further rearrangement is impossible. The same authors found that if tertiary bases are heated with a small excess of dimethyl sulfite at 100–140°, high yields of corresponding sulfonate salts result. The following explanation can be offered. If methyl sulfite ions can be alkylated by dimethyl sulfite, it probably can be alkylated by methyl methanesulfonate as well, as the latter exhibits at least as much alkylating power (*e.g.*, toward iodides and amines). This would, therefore, imply the possibility of route 11 as a final step, in which sulfonic ester converts alkyl sulfite into alkyl sulfonate. It could also explain why the yields of the Bissinger rearrangement should be rather low; the actual catalyst in the reaction might easily be destroyed by the product (sulfonic ester) which it helps to form.

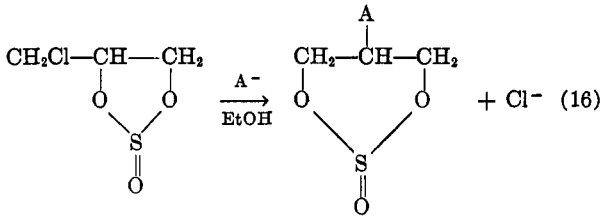
Voss and Wulkan have reported (239) that the action of dimethyl sulfite on amino acids results in alkylation on the nitrogen and esterification of the carboxylic group, as shown for alanine in the following equation.

$$(CH_3O)_2SO + NH_3^+\text{—}CHCH_3\text{—}COO^- \xrightarrow[95\%]{130^\circ} (CH_3)_3N^+\text{—}CHCH_3\text{—}CO_2CH_3 \cdot CH_3SO_3^- \qquad (15)$$

The product is a trimethylammonium salt of methanesulfonic acid. Simultaneously a certain part of dimethyl sulfite rearranges to methyl methanesulfonate. This appears to be another example to which Bartlett's mechanism applies. As the reaction conditions were such that the amino acids gradually took part in the

reaction, it is likely that sulfonic ester product contributed to the alkylation of the nitrogen (route 10).

In an attempt to isomerize 1,4-butylene sulfite, Gilles (98) obtained pure tetrahydrofuran in 76% yield. The proposed mechanism was essentially similar to routes 3 and 5 followed by an internal cyclization. A novel reaction of substituted cyclic sulfites discovered by Ben-Ishay (16, 17) constitutes an interesting illustration of reaction paths already discussed. The five-membered cyclic sulfite of 1-chloropropane-2,3-diol rearranges to a six-membered ring on gentle heating with sodium phenolate or cresolate. Actually both possible isomers result, but if A is the anion of 7-theophillin



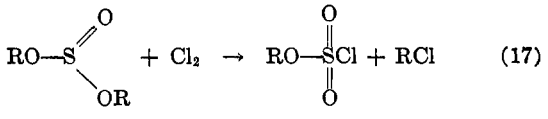
the final product is exclusively a substituted trimethylene sulfite. It was suggested that the mechanim should be a backsides displacement of a chloride ion by the sulfite group, involving the formation of a bridged carbonium ion which reacts further with A^-. It is improbable though that an electron-withdrawing sulfite group would favor the dissociation of a chloride ion. In analogy with other O-alkylations it is preferred, therefore, to formulate the reaction as a nucleophilic substitution on either of the three electropositive carbon atoms (preferentially the one carrying a halogenated methyl group) and simultaneous migration of the formed sulfite ion.

G. REACTION WITH GRIGNARD REAGENT

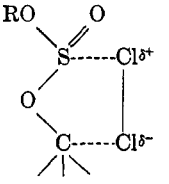
The reaction of Grignard compounds with aliphatic and aromatic sulfites, similarly as with thionyl chloride, yields symmetrical sulfoxides (18, 99, 215). The alkyl or aryl groups introduced in the sulfoxide group originate from the Grignard reagent. According to Szmant and Emerson (219) alkylation on the sulfur proceeds in two steps, the second being comparable with Grignard's reaction for sulfinic acids.

H. OXIDATION

It has been discovered by Levaillant (136) that chlorine passed into aliphatic sulfites in the cold readily produces equimolecular amounts of alkyl chlorosulfonate and alkyl chloride.



Carried out at about 130° the reaction continues with excess of sulfite to give dialkyl sulfate in high yield (see section IIIB). A number of halogenated alkyl chlorosulfonates were obtained from corresponding sulfites *via* reaction 17 in the same manner, sometimes only when light was applied (137, 138, 139). In later years Cross and Gerrard (59) investigated this reaction with the sulfite of optically active *sec*-octyl alcohol and observed that inverted *sec*-octyl chloride is formed, accompanied by considerable loss in rotatory power. Similar phenomena were observed when bromine was used. Two mechanisms were proposed: one predominating and involving electrophilic attack by halogen on the sulfur atom followed by a backside attack on the octyl group by a chloride ion and so inverting the configuration; the other involving a simultaneous approach of sulfur and carbon centers by a chlorine mole-



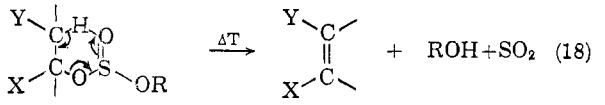
cule resulting in retention of configuration and thereby reducing the rotatory power of the product.

Oxidation of organic sulfites with agents such as nitrogen dioxide, ozone, and benzoyl peroxide had only the effect that the sulfite group was destroyed and the nearest carbon atom attacked (11). However, with the use of permanganate, oxidation to a corresponding sulfate seems feasible. Dibutyl sulfate was thus obtained in 55% yield in glacial acetic acid solution (70). More recent examples are the oxidation of bis-(2-methyl-2-nitropropyl) sulfite by refluxing in acetone with potassium permanganate, yield 75% (129), and of the cyclic sulfites of several glycols by a rapid exothermic reaction with calcium permanganate in aqueous acetic acid in the cold (29, 84).

I. PYROLYSIS

Prior to 1954 when Price and Berti (19, 176, 177) published a first systematic investigation on this subject, only scattered results of pyrolytic experiments occur in the literature. It appears that symmetrical and asymmetrical sulfites decompose on heating primarily to olefins and alcohols with elimination of sulfur dioxide. Methyl cholesteryl sulfite, for example, pyrolyzes to 3,5-cholestadiene at 185° (19). The reactions are generally characterized by a rather low temperature (200–250°). Because of this the yields are often 70 to 80%, and in many cases the final product was reported as rather pure. Berti (19) has investigated the stereospecificity of the reaction by pyrolyzing both isomers of methyl 2-phenylcyclohexyl sulfite. His supposed results have been questioned by Eliel, McCoy, and Price (69) and later on by Bordwell and Landis (25), who examined the same compounds as well

as isomers with a *t*-butyl, tosyl, or thio-*p*-cresyl group as substituent in the 2-position of the cyclohexane ring. In a number of cases, but not always, pyrolysis proceeds by an intramolecular *cis*-elimination. This would point to a mechanism similar to other ester pyrolyses for



which the transition state is thought to be a quasi six-membered ring with a concerted shift of electrons taking place, but from the fact that *trans*-eliminations occur occasionally and also eliminations under ring contraction, it was concluded that an ion-pair mechanism (formation of alkyl sulfite ion in the transition state) is an attractive alternative. Other examples of *trans*-eliminations have been found for the methyl sulfite of *erythro*-3-substituted-2-butanol (26). A case of ring contraction has also been found in a study on a few terpenic sulfites (67); methyl bornyl sulfite rearranges to 1-camphene at 200° (78%). Table I shows a compilation of symmetrical sulfites from the literature, decomposing to olefins according to equation 18. X and Y refer to substituents in the given schematic drawing. For lower homologs in the aliphatic series, formation of ethers has been observed (179, 211, 236). This has also been reported for dicyclohexyl sulfite (141) and methyl cyclohexyl sulfite (116). If a propyl group is substituted in the cyclohexane ring in 4-position, olefins again result (145). A few sulfites containing benzyl or benzhydryl groups gave ethers (116) which is "reasonable" as in these cases an α-hydrogen atom is not available for abstraction. On the whole, however, the data seem too scarce to allow a conclusion about the factors causing this different mode of decomposition.

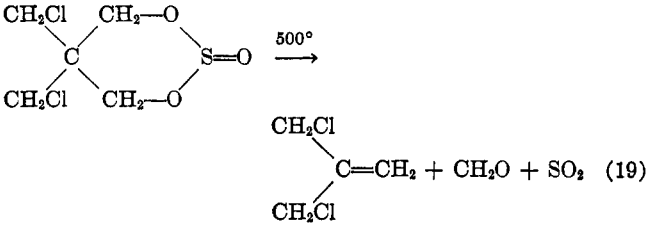
TABLE I

OLEFINS OBTAINED BY PYROLYSIS OF SULFITES
(SEE EQUATION 18; R CONSTITUTING A SYMMETRICAL SULFITE)

Product		Temperature, °C.	Yield, %	References
X	Y			
H	n-C_3H_7	200	50	(176)
H	n-C_5H_{17}	310	—	(48)
H	C_6H_5	250	50[a]	(176)
H	$CH_2C_6H_5$	260	45	(48, 176)
H	o,p-$(CH_3)_2C_6H_3$	290	72	(109)
n-C_3H_7	H	200–240	70–80	(176)
$CO_2C_2H_5$	H	400–500	Low	(196)
C_6H_5	H	130	100	(176)
CH_3	C_6H_5	235	125[b]	(176)

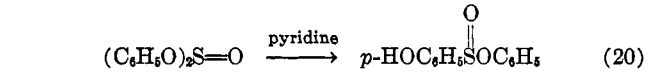
[a] 25% of corresponding ether also produced. [b] Ratio of propenylbenzene–alkyl benzene = 1:1.

Up to the present only two cases are known in which a cyclic sulfite with loss of sulfur dioxide goes to the corresponding oxide. Thus, 1,2-dimethylethylene oxide was prepared from 2,3-butylene sulfite (64) and an oxetane was obtained after pyrolysis of pentaerythrityl disulfite (147, 242). Other 2-substituted-1,3-propylene sulfite and 1,2-glycol sulfites have been tried (147, 177, 242) without success. 2,2-Dimethyl-1,3-propylene sulfite resisted pyrolysis up to 500° (242) while 2,2-bis-(chloromethyl)-1,3-propylene sulfite decomposed smoothly at this temperature to give 91% of 3-chloro-2-chloromethyl-1-propene (155).



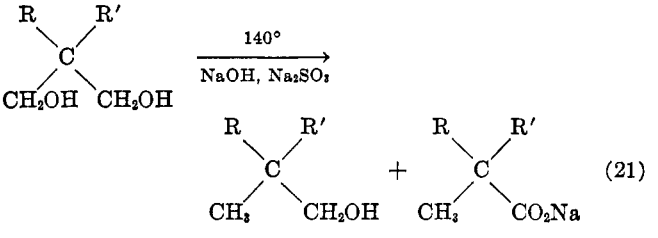
J. MISCELLANEOUS REACTIONS

Libermann and Rouaix (145) have reported a remarkable reaction for aromatic sulfites in the presence of small amounts of pyridine. Diphenyl sulfite heated in boiling xylene yielded about 60% of phenyl hydroxybenzenesulfinate, the position of the hydroxyl group probably being *para*.



Bis-(β-naphthyl) sulfite reacts in a similar way. The mechanism of this rearrangement has not yet been elucidated.

1,3-Glycols have recently been observed to rearrange to a monoalcohol when heated with a slurry of water, sodium hydroxide, and sodium sulfite (60). The proposed mechanism involved a 1,3-hydride shift and elimination of one of the hydroxyl groups. The resulting aldehyde would then go to the final products *via* a Cannizzaro reaction. For the corresponding cyclic sulfites, reacting likewise in the absence of sodium sulfite, a similar shift was suggested. Considering, however, that the esters under the conditions quoted will hydrolyze instantaneously, it seems unjustified to distinguish between the reaction of the sulfite and that of the glycol itself.



IV. PHYSICAL PROPERTIES; THE NATURE OF THE S=O BOND

In general, aliphatic as well as aromatic open-chain sulfites are liquids at room temperature and tend to

become viscous oils with increasing molecular weight. When pure they are usually colorless and almost odorless. A notable exception forms *o*-phenylene sulfite which is highly lacrimogenous (1). Solids are mainly found among the cyclic esters and have a relatively low melting point.

Strecker and Spitaler (216) attempted in 1926 to confirm the molecular constitution of various oxy derivatives of aliphatic sulfur compounds by means of refractivity data. Starting from molecular refractivities and subtracting contributions from alkyl groups, they deduced values for the "inorganic group" in each compound. It appeared that sulfoxides ("sulfonyl" group) and sulfones ("sulfuryl" group) have a very similar group refractivity. A similar correspondence exists between sulfites and sulfates although their value is somewhat higher. The value for sulfonic esters lies about half-way between these two sets. This result correlated nicely with differences in the accepted configuration for these compounds.

More physical constants of sulfites were determined by Vogel and Cowan (229, 230) who have calculated structural constants from molecular refractivities, refraction coefficients, and parachor values (for parachors of cyclic compounds see (7)). In later years (231) bond refractions and bond parachors were introduced. The authors concluded from their values that there are no indications for assuming a covalent double bond in organic sulfites. Similar conclusions were reached as regards the nature of oxy-bonds in, *e.g.*, sulfoxides and sulfones. On the basis of diamagnetic susceptibility measurements it was suggested (56) that sulfites are resonance hybrids of the structures

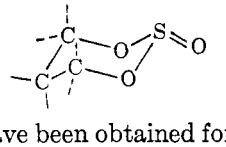
Originally, under the influence of Lewis' octet theory, dative links were assumed throughout for the nature of oxy-bonds in oxy-acids of phosphorus, sulfur, and chlorine and likewise for their organic derivatives. Nowadays this formulation is no longer favored. Conclusive experimental data about bond distance, bond energy, and dipole moment indicate that the sulfur–oxygen link is a nearly covalent double bond (173) in which 3d-orbitals of sulfur must play an important role (164). Although sulfites have not been considered in particular, the general validity of this conclusion seems hardly questionable. Evidence for a covalent double bond in sulfites was presented by Simon and Kriegsmann (207) from infrared and Raman spectroscopic studies.

Dipole moment data (6, 119, 180, 194, 195, 218) have not been discussed in connection with the nature of the S=O bond but do seem to be consistent with a sulfite group of pyramidal configuration (4, 194). Recent investigations of n.m.r. spectra have clearly demonstrated the stable nonplanar configuration in cyclic sulfites. Ethylene sulfite showed a nonequivalence of all its protons, as contrasted with ethylene sulfate (180); likewise a 2-substituted trimethylene sulfite, which was compared with the corresponding carbonate (5). The spectra of some dialkyl sulfites have also been analyzed (73) and commented upon (241). From Raman spectroscopic studies (156, 209, 232) the various modes of vibration in simple molecules could be assigned on the basis of a pyramidal sulfite group.

Much of the available infrared data (16, 55, 65, 150, 219) has been reviewed by Bellamy (14, 15). The characteristic S=O stretching frequency lies near 1200 cm.$^{-1}$. This position is well distinct from that of sulfoxides (about 1050 cm.$^{-1}$), sulfinic esters (about 1130 cm.$^{-1}$), or the symmetrical and asymmetrical vibration modes of isomeric sulfonic esters (1150 and 1350 cm.$^{-1}$, respectively). Bellamy's embarrassment as regards the insensitivity of the absorption frequency to the effects of ring strain may seem premature, as there appears to be no ring strain in the cyclic sulfites concerned; thermochemical measurements (63, 169) show that the heats of hydrolysis of five- and six-membered rings equal those of comparable open-chain compounds.

V. Miscellaneous Properties and Applications; Isomerism due to the Nature of the Sulfite Group

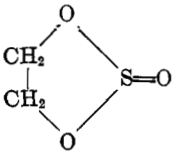
Although Voss and Blanke (236) suggested in 1931 that the coordination of oxygen atoms around the central sulfur atom in a sulfite group might be noncoplanar, analogous to the configuration of sulfoxides and sulfinic esters, this was confirmed by experiment only some twenty years later. In 1952, Herzig and Ehrenstein (114) isolated two isomers of the cyclic sulfite of 3α-chloro-5,19-dihydroxyethiocholanic acid ethyl ester. The existence of isomeric forms could only be explained by assuming asymmetry in the sulfite group as this would enable the exocyclic S=O bond in this compound to take two different configurational positions relative to the steroid skeleton to which it is condensed. A case of isomerism in a simple cyclic compound was discovered by de la Mare and Klyne and co-workers (150) a few years later. Trimethylene sulfite with chlorine substituted in 2-position was shown to occur in *cis–trans* isomers. Infrared spectra of these and of a cyclic sulfite of 5β-cholestane-3β:5-diol were discussed in connection with the probable conformation of the ring and orientation of the S=O bond.



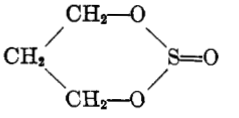
Similar isomers have been obtained for a five-membered ring (180). In addition to this, information about the

TABLE II

SUBSTITUTED FIVE- AND SIX-MEMBERED CYCLIC SULFITES



Substituents at		References
C-1	C-2	
—	CH_2Cl	(16)
—	C_2H_3	(20)
—	$CH(OC_2H_5)_2$	(204)
CH_3	CH_3	(55, 197)
CH_3	C_2H_5	(55)
C_2H_5	C_2H_5	(55)
CH_2CO_2R	CH_2CO_2R	(135)
C_6H_5	C_6H_5	(177, 183)
cis-1,2,3,4-Tetramethyl-cyclobutylene 1,2-sulfite		(58)



Substituents at			References
C-1	C-2	C-3	
—	—	CH_3	(167)
—	C_2H_5	n-C_3H_7	(167)
—	CH_3, NH_2	—	(125)
CH_3	—	CH_3, CH_3	(167)
—	NO_2	—	(175)
—	C_2H_5, NO_2	—	(226)
—	R, NO_2	—	(146)
—	CH_2Cl, NO_2	—	(74)
—	NR_2	—	(175)
—	C_6H_5O	—	(16)
—	2-Piperidyl	—	(52)
p-$NO_2C_6H_4$	NHAc	p-$NO_2C_6H_4$	(206)

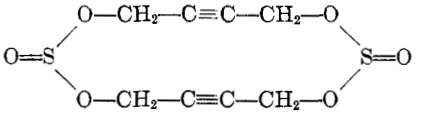
structure of the sulfite group has been supplied by physicochemical studies (see previous section).

In Table II a number of five- and six-membered cyclic sulfites are compiled. It is highly surprising that *cis–trans* isomerism similar to the cases mentioned has not been noticed for any of these compounds. The same applies to almost any cyclic sulfite described hereafter in this section.

Sulfites of diols have often been isolated by accident in attempts to replace hydroxyl groups by chlorine atoms. After all, they have sometimes shown to be of interest for very divergent reasons. Thus, *d*- or *l*-2,3-butanediol could readily be separated from the *meso* isomer *via* the corresponding sulfites (197) owing to their difference in boiling point. One wonders whether hydrobenzoin and isohydrobenzoin could be separated with more ease in a similar manner by fractional crystallization. The respective sulfites have been investigated by various authors (130, 177, 183).

Sulfites of chloramphenicol and closely related compounds are known (163, 206) and have been patented for their antibiotic properties. The sulfites of 6-substituted-16α-17α-dihydroxyprogesterone show endocrine activity (83). The possibility of forming the cyclic sulfite of a polycyclic dihydroxy compound has in some cases been advanced as evidence for diaxiality of two hydroxyl groups (126, 174). In the cyclohexane ring system this seems to hold only for hydroxyl groups in 1–3 position. Cyclization with hydroxyls positioned at adjacent carbon atoms is possible when both are equatorial as in *trans*-1,2-cyclohexanediol (75, 177) or methyl 4:6-O-benzylidene-α-D-glucoside (117) but apparently also if one hydroxyl is axial as in *cis*-1,2-cyclohexanediol (75, 177) or styracitol (8).

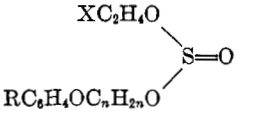
Other types of dihydroxy compounds from which cyclic sulfites are known are 2-substituted-1,4-anhydroxylitol (124), *cis*-3,4-thiolanediol (178), and 2-butene-1,4-diol (187). However, 2-butyne-1,4-diol cyclizes to a dimeric sulfite (182).



From 1,4-cyclohexanediol only a polymeric sulfite could be obtained (168). Products of the same kind result by the action of thionyl chloride and pyridine on alkanediols in which the hydroxyl groups are separated by four or more carbon atoms such as 1,10-decanediol. These long-chain polymers (167) and some other aliphatic sulfites (166) have been patented as stabilizers for cellulose ethers and esters.

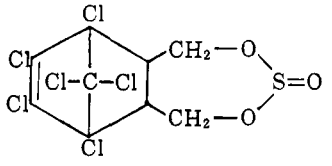
When polyhydric alcohols are heated with excess thionyl chloride, compounds may be obtained containing two or more sulfite groups in ring form in one molecule. Thus, disulfites have been prepared of pentaerythritol (100, 101), styracitol (8), diethyl mucate (130), and erythritol (148), while mannitol yields a trisulfite (130, 148).

Since 1929 when a first report was published (120) about pesticidal properties of sulfites, a growing interest, reflected in the patent literature, is noticeable for certain types of compounds (85, 112, 223, 224, 225). Particularly the toxicity to mites displayed by a great variety of halogenated asymmetrical sulfites has led to the syntheses and examination of a large series of compounds (108, 110). A study of the relation between chemical structure and activity toward the two-spotted spider mite (111) shows that one "small" radical containing halogen increases the toxicity markedly over the unsubstituted



compound while the other radical, preferably of considerable molecular shape, can be varied widely in structure without serious repercussions on the toxicity; inexpensive aryloxyalkanols have been chosen for this purpose. If the sulfur atom in these mixed sulfites constitutes a center of asymmetry, one would expect diastereoisomers to exist for sulfites having a second asymmetrical center (*e.g.*, carbon) in the rest of the molecule. Observations on this point have not been reported.

Another type of pesticidal sulfites is derived from unsaturated polycyclic diols (82) such as thiodan.



Of the latter compound (190, 191) and some of its analogs (188, 192) two isomeric forms are known. Reimschneider and Wuscherpfennig (193, 194, 195) have attributed their existence to the pyramidal sulfite group. They also considered the dipole moments and possible conformations of thiodan and other seven-membered cyclic sulfites.

Finally, the following properties have also been claimed for typical sulfites: regulation of plant growth (186), color stabilization (165), solving power for sulfur dioxide (228) and plastics (171), and plasticizing properties (166, 171). Linear condensation polyesters can be prepared from dicarboxylic acids and ethylene sulfite as starting materials (54).

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VI. References

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