

E2 eliminations from esters. Moreover, *cis-trans* isomeric amines with rigid five-membered rings and with flexible seven-membered rings, the exhaustive methylation of which has not been studied as yet, should also be used for comparison purposes.

## VII. The Saytzeff and Hofmann Rules

Examination of the E1 and E2 eliminations described above in order to determine whether they obey one of the two rules shows that the relationships that have until now been regarded as generally valid<sup>[41]</sup> do not hold. E1 eliminations do not all follow the Saytzeff rule, nor do E2 eliminations from halides and esters of sulfonic acids, and the Hofmann rule in the E2 mechanism is not predominantly restricted to onium compounds. However, the behavior of the cycloalkane derivatives clearly shows that the steric structure of a molecule in the ground state can have a decisive effect on the mode of reaction.

The Saytzeff rule follows from those E1 eliminations that proceed rapidly with participation of tertiary hydrogen. When the steric conditions for the participation of tertiary hydrogen are not satisfied, the Saytzeff rule may still be more or less strictly obeyed if a hydride shift in the initially formed ion leads to a tertiary carbonium ion. The stabilization of this ion by loss of a proton to give a trisubstituted or tetrasubstituted "ethylene" then competes to a greater or lesser degree with stabilization of the initially formed primary or secondary carbonium ion by deprotonation, which leads to an olefin having a less highly alkylated double bond. For thermodynamic reasons, eliminations leading to equilibria obey the Saytzeff rule.

[41] See [14], p. 733, top of the left-hand column.

The Hofmann rule is obeyed with statistical probability when all the hydrogen atoms available for elimination are equally suitable; in the least favorable case, *i.e.* when there is a choice between a CH<sub>3</sub> and a CH<sub>2</sub> group, 2/3 of the product is Hofmann hydrocarbon. The relative yield of the Hofmann hydrocarbon can be higher if the reactivity increases with the number of protons on a group. This is so *e.g.* in the case of tertiary hydrogen, which has an anionic character owing to the inductive effect; this hydrogen remains intact in E2 eliminations, which are induced by a proton acceptor, and even in E1 reactions it may be taken up by the solvent to a smaller extent than "primary" or "secondary" hydrogen. Thus vicinally *trans*-alkylated and vicinally *cis*-alkylated cycloalkyl *p*-toluenesulfonates undergo *trans* E2-elimination involving the secondary hydrogen, even when the tertiary *trans*-hydrogen occupies the sterically favorable coplanar positions (see Section V).

If there is a choice between secondary and primary hydrogen, no generalizations can be made in view of the small statistical superiority of the primary hydrogen. The attack on a given hydrogen atom may be facilitated or hindered by steric factors; the elimination will be accelerated or retarded, depending on whether the hydrogen and the leaving group are more or less coplanar. The importance of electronic effects as compared with steric effects is unknown, since the steric factors can only be roughly estimated in general. The importance of bulk in E2 reactions in the aliphatic series has been discussed by *H. C. Brown*<sup>[42]</sup>.

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German version: *Angew. Chem.* 79, 555 (1967)

Translated by Express Translation Service, London

[42] *H. C. Brown* and *I. Moritani*, *J. Amer. chem. Soc.* 78, 2203 (1956); *H. C. Brown* and *R. L. Klimisch*, *J. Amer. chem. Soc.* 88, 1425 (1966).

## The Chemistry of Bunte Salts

BY H. DISTLER [\*]

*Bunte salts can be obtained, not only from alkyl halides and sodium thiosulfate, but also from compounds containing activated multiple bonds, and sodium thiosulfate. The Bunte salts prepared by the new method, contrary to earlier observations, are cleaved by alkalis into the unsaturated starting compounds and sodium thiosulfate. This reaction, which is used for the fixation of unsaturated compounds (e.g. to cellulose), and other reactions of the Bunte salts are discussed. The industrial applications and biological properties of the Bunte salts are also mentioned.*

### 1. Introduction

Alkali metal *S*-alkylthiosulfates and *S*-arylthiosulfates are known as "Bunte salts". Since sodium *S*-ethylthiosulfate<sup>[1]</sup> was first prepared by *Bunte* (1874), many articles dealing with the chemistry of this class of substances have been published<sup>[2]</sup>.

When *Bunte* synthesized sodium *S*-ethylthiosulfate, which he obtained by heating an aqueous solution of sodium thiosulfate with ethyl bromide, his main

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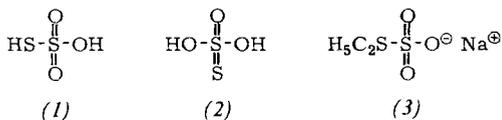
[1] *H. Bunte*, *Chem. Ber.* 7, 646 (1874).

[2] *B. Milligan* and *J. M. Swan*, *Rev. pure appl. Chem.* 12, No. 6, p. 72 (1962).

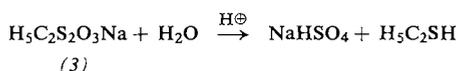
object was to find conclusive proof of the constitution of thiosulfuric acid, which was still very uncertain at



that time. Of the possible isomeric forms (1) and (2), the synthesis and chemical behavior of sodium *S*-ethylthiosulfate are compatible only with a derivative

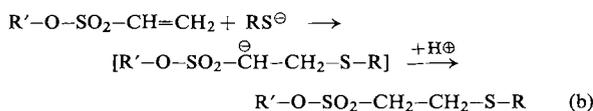


of the structure (1). This is shown in particular by *Bunte's* observation that sodium *S*-ethylthiosulfate gives ethylthiol on acid hydrolysis.

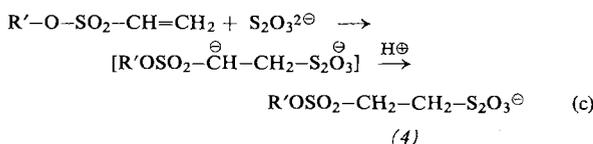


The structure (3) was confirmed by a series of syntheses and secondary reactions, and also agrees with the results of UV<sup>[3]</sup>, Raman, and IR measurements<sup>[4, 108]</sup>.

The thiosulfate anion should contain different nucleophilic centers, and the nucleophilic strength should be greatest on the sulfur atom. It seemed desirable to check this experimentally, since it is well known that many nucleophiles, *e.g.* thiolate, add smoothly to compounds containing activated double bonds. The addition of thiolate ion to vinylsulfonic acid derivatives may be cited as an example [eq. (b)]<sup>[5]</sup>.



We found that, in general, the addition of thiosulfate ions to vinylsulfonic acid derivatives proceeds smoothly and almost quantitatively in accordance with equation (c), to give Bunte salts (4) that crystallize well from water. The same reaction conditions were then used in an attempt to add thiosulfate ion to other



compounds containing activated double bonds, such as acrylic and methacrylic acids and their derivatives, as well as methyl vinyl ketone. *Kerber and Starnick*<sup>[6]</sup> carried out an independent study of the direct addition of sodium thiosulfate to compounds containing activated double bonds and obtained identical results.

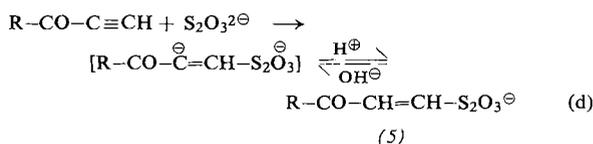
[3] *H. Ley and E. König*, *Z. physik. Chem. B* 41, 379 (1938).

[4] *A. Simon and D. Kunath*, *Chem. Ber.* 96, 157 (1963).

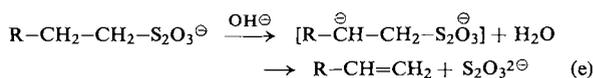
[5] *H. Distler*, *Angew. Chem.* 77, 291 (1965); *Angew. Chem. internat. Edit.* 4, 300 (1965).

[6] *R. Kerber and J. Starnick*, *Tetrahedron Letters* 1966, 3007.

These authors ultimately extended the method to compounds containing activated triple bonds, which give Bunte salts (5) containing a C–C double bond.



In the study of the reactions of Bunte salts obtained by the direct addition of thiosulfate to activated multiple bonds, a surprising result was obtained on cleavage with aqueous alkali. Acid hydrolysis of Bunte salts yields thiols<sup>[1]</sup>, alkaline degradation was reported to yield sodium sulfite<sup>[7, 8]</sup>, alkylsulfenic acids, alkylsulfonic acids, disulfides, thiocarboxylic acids<sup>[9, 10]</sup>, *etc.* However, we have found that Bunte salts obtained by direct addition of thiosulfate to activated multiple bonds are converted back into the

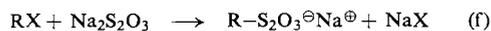


unsaturated starting compounds on treatment with aqueous alkalis. This behavior is particularly interesting and significant for the fixation of unsaturated compounds on fibers, *e.g.* cellulose.

## 2. Methods for the Preparation of Bunte Salts

### a) Bunte Salts from Alkyl Halides and Alkali Metal Thiosulfate

The original method<sup>[1]</sup> for the synthesis of sodium *S*-alkylthiosulfates consists in the reaction of alkyl halides with sodium thiosulfate in aqueous solution at high temperature [see equation (f)].



This method, which was frequently used (see<sup>[1, 2, and 11–18]</sup>), was extended to the preparation of Bunte salts

[7] *A. Gutmann*, *Chem. Ber.* 40, 2818 (1907).

[8] *A. Gutmann*, *Z. analyt. Chem.* 66, 225 (1910).

[9] *T. S. Price and D. F. Twiss*, *J. chem. Soc. (London)* 93, 1395 (1908).

[10] *T. S. Price and D. F. Twiss*, *Chem. Ber.* 41, 4375 (1908).

[11] *W. Spring and E. Legros*, *Chem. Ber.* 15, 1938 (1882).

[12] *D. T. Gibson*, *J. chem. Soc. (London)* 1930, 12.

[13] *R. H. Baker and C. Barkenbus*, *J. Amer. chem. Soc.* 58, 262 (1936).

[14] *H. E. Westlake and G. Dougherty*, *J. Amer. chem. Soc.* 63, 658 (1941).

[15] *U. Weiss and S. Sokol*, *J. Amer. chem. Soc.* 72, 1687 (1950).

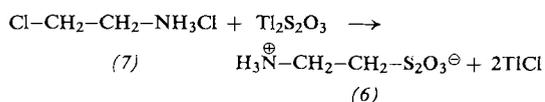
[16] *D. A. Peak and T. J. Watkins*, *J. chem. Soc. (London)* 1951, 3292.

[17] *Z. El Heweki and E. Taeger*, *J. prakt. Chem.* 7, 191 (1958).

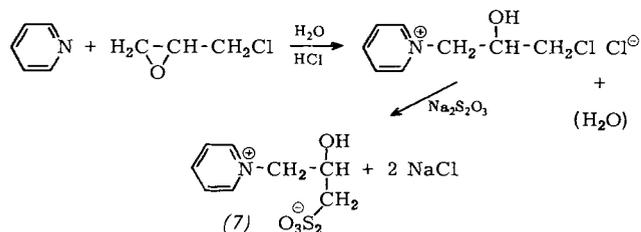
[18] *B. Milligan and J. M. Swan*, *J. chem. Soc. (London)* 1961, 1194.

from secondary alkyl halides [19,13,20-22]. Tertiary alkyl halides apparently do not react with sodium thiosulfate. *Lecher* and *Hardy* [23] found it advantageous to use thallium(I) thiosulfate instead of sodium thiosulfate, since the isolation of the readily soluble Bunte salt is facilitated by the low solubility of the thallium chloride formed.

Even alkyl halides RX with a very wide variety of substituents in the residues R react with sodium thiosulfate – generally without side reactions. For example, alkyl halides that also contain primary [23-27], secondary [22,28], or tertiary amino groups [16,27,20,22,23] can be converted into Bunte salts. These can sometimes be isolated as inner salts (6) [160].



Betaine-like compounds can also be obtained from pyridine, chloroepoxypropane, and sodium thiosulfate [29].



Halogenated fatty acid derivatives of amines [30,31,15] also undergo this reaction. This class of substances was extensively studied in connection with the synthesis of thioctic acid (lipoic acid) [32-35] and its intermediates [36-39]. Dyes contain-

[19] *B. Milligan* and *J. M. Swan*, *J. chem. Soc. (London)* 1961, 5552.

[20] *H. Brettschneider* and *W. Sachsenmaier*, *Mh. Chem.* 84, 619 (1953).

[21] *S. Ose* and *Y. Yoshimura*, *J. pharmac. Soc. Japan (Yakugakuzasshi)* 77, 730 (1957); *Chem. Abstr.* 51, 17856 (1957).

[22] *K. Koczka* and *G. Fodor*, *Acta chim. Acad. Sci. hung.* 13, 89 (1957); *Chem. Abstr.* 52, 12845 (1958).

[23] *H.Z. Lecher* and *E.M. Hardy*, *J.org.Chemistry* 20,475 (1955).

[24] *D. H. Ball*, *J. M. Williams*, and *L. Long*, *J. org. Chemistry* 28, 1589 (1963).

[25] *D. L. Klaymann* and *W. F. Gilmore*, *J. med. Chemistry* 7, No. 6, p. 823 (1964).

[26] *P. Schlack*, German Pat. Appl. K 7123/12 o (Dec. 23, 1944), Kunstseidefabrik Bobingen.

[27] *H. Brettschneider*, *Österr. Akad. Wiss. Math. Naturwiss. Kl. S.-B. Abt. IIB* 159, 372 (1950); *Chem. Abstr.* 47, 6860 (1953).

[28] *P. Schlack*, German Pat. 869006 (March 2, 1953); *Chem. Abstr.* 48, 11485 (1954).

[29] *W. Gündel*, German Publ. Pat. Appl. 1205973 (Feb. 2, 1963), Dehydag.

[30] *B. Milligan* and *J. M. Swan*, *J. chem. Soc. (London)* 1959, 2969.

[31] *A. J. Speziale* and *P.C. Hamm*, *J. Amer. chem. Soc.* 78, 5580 (1956).

[32] *Y. Deguchi* and *K. Nakanishi*, *J. pharmac. Soc. Japan (Yakugakuzasshi)* 83, 701 (1963).

[33] *Y. Deguchi* and *K. Nakanishi*, *J. pharmac. Soc. Japan (Yakugakuzasshi)* 83, 704 (1963).

[34] *Y. Deguchi* and *K. Miura*, *J. pharmac. Soc. Japan (Yakugakuzasshi)* 83, 708 (1963).

[35] *Y. Deguchi* and *K. Miura*, *J. pharmac. Soc. Japan (Yakugakuzasshi)* 83, 717 (1963).

[36] *Fujisawa Pharm. Co. Ltd.*, *Jap. Pat.* 22860/1963.

ing thiosulfate groups, which may carry various substituents, are being produced on the industrial scale [40-60]. It is reported [61] that sodium thiosulfate reacts only with terminal halogen atoms in polychlorinated hydrocarbons. Chlorinated ethers [62-65] and thioethers [66,67] as well as various substituted benzyl halides [68,69] also react under the classical conditions of the synthesis of Bunte salts.

The alkyl halide is made to react with aqueous sodium thiosulfate solution, usually in the presence of a solubilizing agent such as methanol or ethanol. The reaction is usually complete after one or more hours under reflux. Dioxane may also be advantageously used as the solvent in some cases [70]; aqueous acetic acid has been recommended in particular for aminoalkyl halides [20]. Prolonged heating should be avoided. The reaction mixture generally becomes homogeneous when the reaction is complete. The course of the reaction can be readily followed by determination of the thiosulfate. Isolation of the product is occasionally hindered by the sodium chloride formed in the reaction. The Bunte salts can be purified conveniently by hot extraction with alcohol, in which most of them are readily soluble.

[37] *Fujisawa Pharm. Co. Ltd.*, *Jap. Pat.* 22861/1963.

[38] *Fujisawa Pharm. Co. Ltd.*, *Jap. Pat.* 16461/1963.

[39] *Fujisawa Pharm. Co. Ltd.*, *Jap. Pat.* 9215/1962.

[40] *Farbwerke Hoechst AG.*, *Belg. Pat.* 590397 (May 2, 1960).

[41] *Farbwerke Hoechst AG.*, *Belg. Pat.* 606750 (July 31, 1960).

[42] *Farbwerke Hoechst AG.*, *Belg. Pat.* 593886 (Aug. 8, 1960).

[43] *Sandoz S.A.*, *Belg. Pat.* 606571 (July 26, 1960).

[44] *E. Baier*, *W. Happe*, and *H. Hoffmann*, German Pat. 1146839 (April 11, 1963), *Farbwerke Hoechst AG.*

[45] *Partipharms AG.*, *Netherlands Pat. Appl.* 6464599 (April 24, 1964).

[46] *Farbwerke Hoechst AG.*, *Netherlands Pat. Appl.* 6408206 (July 17, 1964).

[47] *Farbwerke Hoechst AG.*, *Belg. Pat.* 590124 (April 25, 1960).

[48] *Farbwerke Hoechst AG.*, *Belg. Pat.* 590125 (April 25, 1960).

[49] *W. Schultheiss*, *K. Schimmelschmidt*, *H. Hoffmann*, and *E. Baier*, French Pat. 1254830 (April 25, 1960); *Austrian Pat.* 222259 (April 22, 1960); *US.-Pat.* 3098064 (April 18, 1960), all *Farbwerke Hoechst AG.*

[50] *Farbwerke Hoechst AG.*, *Belg. Pat.* 613618 (Aug. 7, 1962).

[51] *Farbwerke Hoechst AG.*, *Belg. Pat.* 608829 (Oct. 4, 1961).

[52] *Farbwerke Hoechst AG.*, *Jap. Pat.* 4043/64 (Feb. 18, 1961).

[53] *B. Milligan* and *J. M. Swan*, *Textile Res. J.* 31, 18 (1961).

[54] *Farbwerke Hoechst AG.*, *Ind. Pat.* 71497 (April 19, 1960).

[55] *Farbwerke Hoechst AG.*, *German Pat.* 1164976 (Feb. 18, 1961).

[56] *Farbwerke Hoechst AG.*, *German Publ. Pat. Appl.* 1164974 (Feb. 23, 1961).

[57] *Farbwerke Hoechst AG.*, *Belg. Pat.* 650713 (July 17, 1964).

[58] *Farbwerke Hoechst AG.*, *German Pat.* 1146839 (July 30, 1960).

[59] *Farbwerke Hoechst AG.*, *Belg. Pat.* 638182 (Oct. 3, 1963).

[60] *Farbwerke Hoechst AG.*, *German Pat.* 1145576 (March 16, 1960).

[61] *H. Bestian* and *G. Theilig*, German Pat. 1003724 (March 7, 1957); *Chem. Abstr.* 53, 15975 (1959).

[62] *Deutsche Hydrierwerke AG.*, *German Pat.* 578568 (June 15, 1933); *Chem. Abstr.* 28, 909 (1934).

[63] *E. Schirm*, *US.-Pat.* 2012073 (Aug. 20, 1935); *Chem. Abstr.* 29, 6670 (1935).

[64] *Soc. pour l'ind. chim. à Bâle*, *Swiss Pat.* 212401 (Feb. 17, 1941); *Chem. Abstr.* 36, 3686 (1942).

[65] *E. M. Fettes* and *E. R. Bertozzi*, *US.-Pat.* 2875182 (Feb. 24, 1959); *Chem. Abstr.* 53, 9726 (1959).

[66] *W.H. Stein*, *J.S. Fruton*, and *M. Bergmann*, *J. org. Chemistry* 11, 692 (1946).

[67] *C. C. Price* and *A. Pohland*, *J. org. Chemistry* 12, 249 (1947).

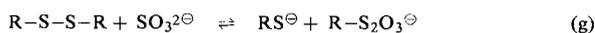
[68] *G. Speroni* and *G. Manelli*, *Gazz. chim. ital.* 70, 472 (1940).

[69] *C. N. V. Nambury*, *J. Sci. Res. Banaras Hindu Univ.* 7, 254 (1956); *Chem. Abstr.* 52, 10930 (1958).

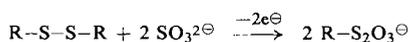
[70] *H. Distler*, unpublished.

## b) Bunte Salts from Disulfides and Alkali Metal Bisulfite

The reaction of a disulfide with sulfite is reversible, as indicated in equation (g) [71-73].

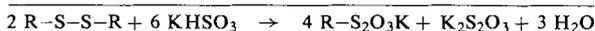
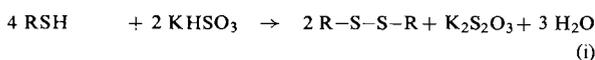


The equilibrium can be displaced in favor of the formation of Bunte salts by the addition of oxidizing agents.



This reaction is utilized in the determination of cysteine and cystine with "Folin's reagent", a phosphorus-tungsten heteropolyacid [74].

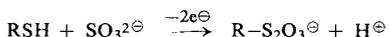
Bunte salts have also been prepared from aromatic disulfides and in particular from amino-substituted disulfides and sodium or potassium bisulfite [75, 76]. Nitro-substituted aromatic disulfides are reported to react similarly and to give excellent yields; depending on the oxidation potential of the intermediate thiol, sodium bisulfite itself can act as the oxidizing agent, promoting almost complete Bunte-salt formation. The course of the reaction can be explained to some extent by the scheme proposed by *Lecher* and *Hardy* [23],



in which the bisulfite, as the oxidizing agent, is brought into the correct relationship with the thiol in equation (i). This would readily explain the very good yields of Bunte salts in the reaction of aromatic disulfides with bisulfites, even in the absence of air [23].

## c) Bunte Salts from Thiols and Alkali Metal Sulfites in the Presence of an Oxidizing Agent

The reaction of thiols with sulfurous acid in the presence of an oxidizing agent, *e.g.* elementary iodine, gives the desired Bunte salts only in poor yields [77].



In reactions with aromatic thiols, *Bernthsen* [78] used air as the oxidizing agent. "Oxidative sulfitolysis", *i.e.* the reaction of sulfurous acid with thiols or disulfides [71, 72], has been studied in protein chemistry with particular reference to the quantitative colorimetric determination of cysteine and cystine with Folin's reagent [74].

[71] *H. T. Clarke*, *J. biol. Chemistry* 97, 235 (1932).

[72] *J. W. H. Lugg*, *Biochem. J.* 26, 2144 (1932).

[73] *F. Micheel* and *H. Emde*, *Z. physiol. Chem.* 265, 266 (1940).

[74] *O. Folin* and *J. M. Looney*, *J. biol. Chemistry* 51, 421 (1922);

*O. Folin* and *A. D. Marenzi*, *ibid.* 83, 103 (1929).

[75] The Clayton Anilin Company Ltd., German Pat. 120504 (1900).

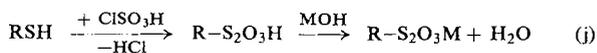
[76] *E. W. McClelland* and *L. A. Warren*, *J. chem. Soc. (London)* 1930, 2690.

[77] *W. Spring*, *Chem. Ber.* 7, 1162 (1874).

[78] *A. Bernthsen*, *Liebigs Ann. Chem.* 251, 1 (1889).

## d) Bunte Salts from Thiols and Chlorosulfonic Acid, Sulfur Trioxide, or SO<sub>3</sub>-Pyridine Complexes

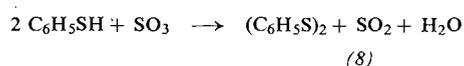
Aliphatic thiols, preferably with long (C<sub>8</sub>-C<sub>18</sub>) branched or unbranched chains, react at low temperatures with chlorosulfonic acid in the presence of an inert diluent such as ether in accordance with reaction (j). Subsequent neutralization with alkali metal hydroxide or ammonium hydroxide yields Bunte salts having surface-active properties [79].



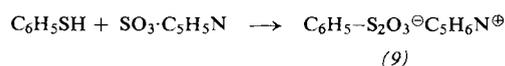
When sulfur trioxide is used instead of chlorosulfonic acid as the sulfating agent, compounds of the same type are obtained at -78 °C in difluorodichloromethane [80]:



At higher temperatures the thiol is oxidized [81] to the disulfide, *e.g.* (8).

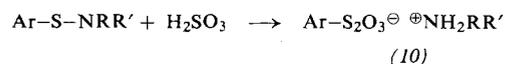


SO<sub>3</sub>-pyridine complexes [82] give quantitative yields of pyridinium *S*-arythiosulfates such as (9) [83, 114].



## e) Bunte Salts from Sulfenyl Chlorides or Amides and Sulfurous Acid

Amides of aromatic sulfenic acids react with sulfurous acid to form *N*-substituted ammonium *S*-arythiosulfates (10) [84].



In most cases it is sufficient merely to digest the amide in concentrated aqueous sulfurous acid with gentle warming. The Bunte salts are readily obtainable by treatment of the ammonium salts (10) with alkali metal hydroxides.

Aromatic sulfenyl chlorides [85] react with alkali metal sulfite in aqueous media to form Bunte salts (11).



[79] *E. L. Dörr* and *Van R. Gärtner*, US.-Pat. 2921952 (July 23, 1956), Monsanto Chem. Co.

[80] *M. Schmidt* and *G. Talsky*, *Chem. Ber.* 94, 1352 (1961).

[81] *R. Schiller* and *R. Otto*, *Chem. Ber.* 9, 1638 (1876).

[82] *E. E. Gilbert*: *Sulfonation and Related Reactions*. Interscience Publishers, New York 1965 (pp. 10, 34, 37, 41, 96, 97).

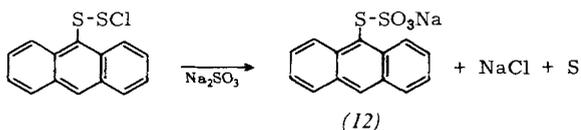
[83] *P. Baumgarten*, *Chem. Ber.* 63, 1330 (1930); German Pat. 530733 (June 7, 1930); *Chem. Abstr.* 26, 152 (1932).

[84] *H. Z. Lecher* and *E. M. Hardy*, US.-Pat. 2706200 (1953).

[85] *Geigy*, Dissertation, Universität München, 1923.

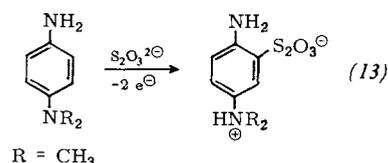
The method is not generally applicable, and is restricted to relatively stable sulfonyl chlorides.

9-Anthryl dithiochloride, which is similar in structure, and which is readily obtainable from anthracene and sulfur monochloride, is converted by aqueous sodium sulfite solution into the sodium salt of *S*-(9-anthryl)thiosulfuric acid (12), with separation of elementary sulfur [86].



#### f) Bunte Salts from Aromatic 1,4-diamines and Thiosulfuric Acid in the Presence of an Oxidizing Agent

Bernthsen [78] observed that in the presence of aluminum thiosulfate and dichromate in acid solution, *p*-dimethylaminoaniline reacts to form *S*-(2-amino-5-dimethylammoniophenyl)thiosulfate (13).

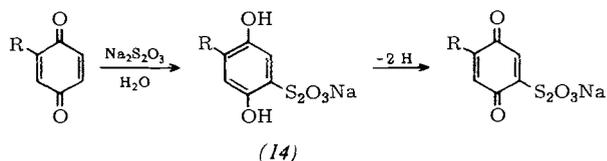


The same inner salt is obtained by the reaction of 4-nitroso-*N,N*-dimethylaniline with aqueous thiosulfuric acid. In this case the nitroso group evidently brings about the substitution of the aromatic amine by thiosulfate [87, 88].

The Bernthsen method has been studied for a number of 1,4-phenylenediamines, and has also been extended to related amines [89-92]. Di- and tetrathiosulfates of 1,4-phenylenediamine can be prepared by addition of the oxidizing agent and thiosulfate [93] in a suitable excess.

#### g) Addition of Thiosulfate to Quinones

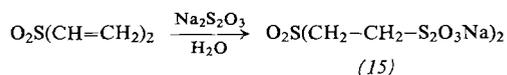
*p*-Quinones add sodium thiosulfate in the presence of aqueous acetic acid [88, 94, 95] to give the sodium salts of substituted *S*-(2,5-dihydroxyphenyl)thiosulfuric acids (14).



The reaction is applicable to quinones in general [96], including 1,4-naphthoquinones [88]. The Bunte salts (14) can be dehydrogenated under mild conditions to quinonethiosulfates [88].

#### h) Addition of Thiosulfate to Divinyl Sulfone

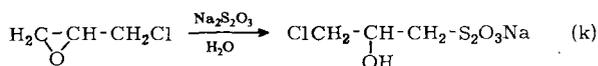
Sodium thiosulfate adds to divinyl sulfone in aqueous bicarbonate solution [97, 98].



Because of the sensitivity of the Bunte salt (15) toward alkali, the reaction is best carried out in the presence of carbon dioxide. Dyes with vinyl sulfone residues have recently been converted into Bunte salts under similar conditions [99]. Under conditions analogous to those suggested by *Stahmann et al.* for the formation of Bunte salts from divinyl sulfone [97], aromatic vinyl sulfones can be converted into aryl-sulfonylethylthiosulfuric acids or their alkali metal salts [100]. They are much more stable toward alkalis than the sulfates of similar structure.

#### i) Reaction of Epoxyalkanes with Sodium Thiosulfate

Whereas 1,2-epoxyalkanes generally react with sodium bisulfite or thiosulfate with ring cleavage to form derivatives of 2-hydroxyethanesulfonic acid (isethionic acid) [101, 102], cases have also been reported in which epoxyalkanes react with thiosulfate in the neutral or weakly alkaline range to give *S*-(2-hydroxyalkyl)thiosulfates [103, 104]. An example of such a reaction is shown in equation (k).



[86] P. Friedländer and A. Simon, Chem. Ber. 55, 3969 (1922).

[87] M. T. Bogert and J. A. Updike, J. Amer. chem. Soc. 49, 1373 (1927).

[88] G. Heller, J. prakt. Chem. 108, 257 (1924).

[89] A. Bernthsen, Chem. Ber. 25, 3128 (1892).

[90] A. Weinberg, Chem. Ber. 25, 1610 (1892).

[91] M. T. Bogert and M. G. Sevag, J. Amer. chem. Soc. 53, 660 (1931).

[92] J. J. Levkoev, N. N. Sveshnikov, J. N. Gorbacheva, N. S. Barvyn, and T. V. Krasnova, Ž. obšč. Chim. 24, 280 (1954); Chem. Abstr. 49, 4627 (1955).

[93] A. G. Green and A. G. Perkin, J. Chem. Soc. (London) 83, 1201 (1903).

[94] W. Alcalay, Helv. chim. Acta 30, 578 (1947).

[95] BASF, German Pat. 175070 (1905).

[96] M. T. Bogert and H. P. Howells, J. Amer. Chem. Soc. 52, 837 (1930).

[97] M. A. Stahmann, C. Golumbic, W. H. Stein, and J. S. Fruton, J. org. Chemistry 11, 719 (1946).

[98] G. C. Tesoro and D. Ferry, US.-Pat. 3153077 (Oct. 13, 1964), (Stevens and Co.).

[99] Farbwerke Hoechst AG., Belg. Pat. 650713 (July 17, 1964).

[100] F. Meininger and E. Hoyer, German Publ. Pat. Appl. 1204666, Farbwerke Hoechst AG. (Oct. 12, 1963).

[101] C. C. J. Culvenor, W. Davies, and N. S. Heath, J. chem. Soc. (London) 1949, 278.

[102] F. Webel, German Pat. 569148 (1931), I.G.-Farben; W. M. Lauer and A. Hill, J. Amer. chem. Soc. 58, 1873 (1936).

[103] Van R. Gaertner, US.-Pat. 2921083 (Jan. 12, 1960); Chem. Abstr. 54, 9331 (1960).

[104] P. Schlack, German Pat. 865597 (Feb. 2, 1953); Chem. Abstr. 48, 10049 (1954).



### a) Behavior of Bunte Salts toward Acids

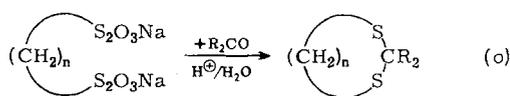
The hydrolysis of sodium *S*-ethylthiosulfate by aqueous acid was correctly recognized by *Bunte* [1] [eq. (n)].



The salt must generally be heated for several hours with dilute acid for complete hydrolysis. Except in special cases (the reaction of sodium benzoilmethylthiosulfate with acid gives 2,5-diphenyl-1,4-dithiin), the method is suitable for the preparation of thiols [15, 17, 23, 110, 111].

A particularly interesting use of Bunte salts is for the preparation of thioacetals and thioketals [14, 112], which are obtained from carbonyl compounds and thiols. The Bunte salts are hydrolysed with acid in the presence of aldehydes or ketones.

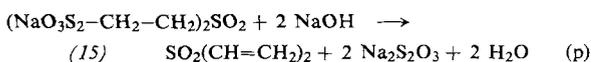
Cyclic thioacetals and thioketals can be obtained in this way by the use of the  $\alpha,\omega$ -alkylenebis(thiosulfates) and formaldehyde or acetone respectively [12, 113] [eq. (o)].



$n = 2, 3$ ;  $\text{R} = \text{H}, \text{CH}_3$

### b) Behavior of Bunte Salts toward Alkalis

According to the literature, the alkaline degradation of Bunte salts is very complex [86]. On the basis of the degradation products (sulfenic acids [7, 8, 114, 115], disulfides, carboxylic acids, thiocarboxylic acids, sulfuric acid, thioethers, and sulfenic acids), several reaction mechanisms, in some cases strongly contradictory, have been proposed [9, 10, 116, 117]. On the other hand, a clear and unambiguous reaction course was found for *S*-alkylthiosulfates, resulting from the addition of thiosulfate to compounds containing activated multiple bonds. In 1946 *Stahmann et al.* [97] observed that the Bunte salt (15) of divinyl sulfone partially decomposes into a substance that readily takes up iodine. In 1961, *Tesoro et al.* [118, 98] assumed that the divinyl sulfone is reformed in accordance with equation (p) during the reaction of the divinyl sulfone



[110] *A. Schöberl and M. Kawohl*, *Mh. Chem.* 88, 478 (1957).

[111] *T. S. Price and D. F. Twiss*, *J. chem. Soc. (London)* 95, 1725 (1909).

[112] *G. G. Stoner and G. Dougherty*, *J. Amer. chem. Soc.* 63, 987 (1941).

[113] *Y. G. Mazover*, *Ž. obšč. Chim.* 19, 843 (1949); *Chem. Abstr.* 44, 3436 (1950).

[114] *A. Dornow*, *Chem. Ber.* 72, 568 (1939).

[115] *K. Fries*, *Chem. Ber.* 45, 2965 (1912).

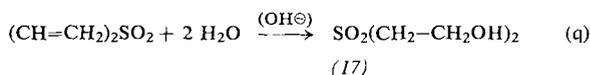
[116] *E. Fromm and F. Erfurt*, *Chem. Ber.* 42, 3816 (1909).

[117] *T. S. Price and D. F. Twiss*, *J. chem. Soc. (London)* 97, 1175 (1910).

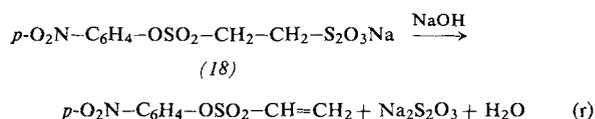
[118] *G. Tesoro, P. Linden, and St. B. Sello*, *Textile Res. J.* 31, 283 (1961).

Bunte salt with cellulose in alkaline media. Bunte salts of vinyl sulfones are reported to behave in a similar manner [119].

So far as we know, no definite proof of the course of the reaction is as yet available, presumably because divinyl sulfone is immediately hydrated in accordance with equation (q) in the presence of aqueous alkali [118]. The resulting bis( $\beta$ -hydroxyethyl) sulfone (17) reacts with divinyl sulfone under the catalytic influence of hydroxide ions to form a water-insoluble adduct having a high molecular weight.



The Bunte salts of aryl vinylsulfonates such as (18), which crystallize very readily, can be quantitatively, converted back into the unsaturated starting compounds by treatment with aqueous alkali [equation (r)].

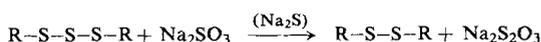
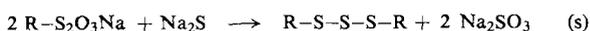


No hydration of the resulting vinylsulfonate under the influence of the hydroxide ions could be observed. Thus the degradation of these Bunte salts (18) in alkaline media is the reverse of their formation [see eq. (1)]. This cleavage evidently takes place with all Bunte salts formed by the addition of thiosulfates to activated CC multiple bonds. Deviations from this rule are to be expected only as a result of secondary reactions, such as hydration of the double bond under the influence of strong alkali [118].

### c) The Alkaline "Fixation" of Bunte Salts on Cellulose and Other Fibers

In the fixation of dyes and unsaturated compounds on fabrics, the functional groups of the fiber react as nucleophiles, *e.g.* OH groups of cellulose, amino and thiol groups of wool, or amide groups in synthetic polyamides.

Whereas reactive dyes undergo a reaction with cellulose that may be regarded as nucleophilic substitution or as nucleophilic addition [159, 120], "Bunte salt dyes" [121] do not react with the fiber. Suitable pretreatment with condensing agents such as sodium sulfide solution is followed by a polycondensation to give a water-fast bond *via* disulfide bridges [cf. eq. (s)].



[119] *G. Tesoro and A. Oroszlan*, *Textile Res. J.* 33, 93 (1963).

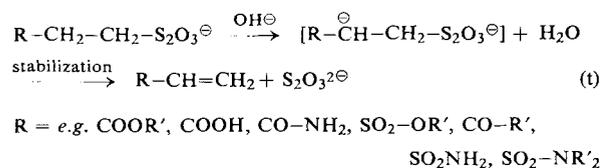
[120] *O. A. Stam*, *J. Soc. Dyers Colorists* 80, 416 (1964).

[121] *K. Schimmelschmidt, H. Hoffmann, and E. Baier*, *Angew. Chem.* 74, 975 (1962); *Angew. Chem. internat. Edit.* 2, 30 (1963).

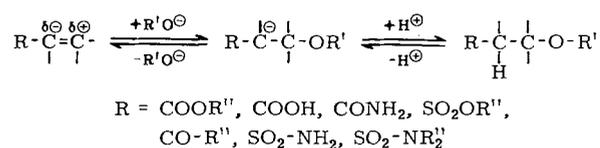
Since "Bunte salt dyes" in general must contain two or more *S*-alkylthiosulfate groups per molecule, it is understandable that condensation with sodium sulfide on the cellulose will lead to a highly cross-linked polydisulfide. Similar highly cross-linked polysulfides were obtained by *Tabushi et al.* [122] with Bunte salts that were prepared *via* chloromethylated polystyrene and sodium thiosulfate and then condensed with sodium sulfide.

Unlike cellulose, wool should react directly with the "Bunte salt dyes" by means of its free SH groups to give disulfides [120, 123].

Bunte salts formed by nucleophilic addition to activated multiple bonds should be particularly suitable for "fixation" in alkaline media. This must be assumed to involve 1,2-elimination of thiosulfate ions in the aqueous alkali [eq. (t)].



The vinyl derivative can again undergo nucleophilic additions. Nucleophilic reagents in general, such as thiols and alcohols, amines, *etc.*, are suitable for this reaction. The compound is then fixed on cellulose in the usual manner. R'SH, R'NH<sub>2</sub> and R'<sub>2</sub>NH add on in the same way.



It is possible in principle to fix many unsaturated monomers that have recently become readily available, and which are often sparingly soluble in water, by masking as Bunte salts as described above. When the Bunte salts derived e.g. from 1,3,5-tris(vinylcarbonyl)-hexahydro-*s*-triazine (16) (triacrylformal) [124] or resorcinol bis(vinylsulfonate) [5] are used, cross-linking effects occur.

#### d) Behavior toward Oxidizing Agents

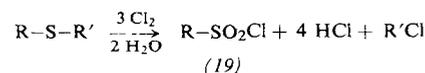
The oxidation of *S*-alkylthiosulfates yields disulfides, sulfonic acids, or their derivatives, depending on the oxidizing agent and the reaction conditions. On oxidation of *S*-ethylthiosulfate with nitric acid, *Bunte* [1] obtained ethanesulfonic acid and sulfuric acid. Hydrogen peroxide leads mainly to disulfides [68, 103, 125-127], as does iodine in hot aqueous

- [122] *J. Tabushi, S. Saito, and R. Oda, J. chem. Soc. Japan, ind. Chem. Sect. (Kogyo Kagaku Zasshi) 67, 478 (1964).*  
 [123] *A. Demian, Rev. Chim. (Bukarest) 16, 255 (1965).*  
 [124] *R. Wegler et al., Chem. Ber. 81, 527 (1948).*  
 [125] *H. E. Westlake and G. Dougherty, J. Amer. chem. Soc. 64, 149 (1942).*  
 [126] *T. F. Twiss, J. chem. Soc. (London) 1914, 36.*  
 [127] *G. G. Stoner and G. Dougherty, J. Amer. chem. Soc. 63, 987 (1941).*

ethanol [68, 103, 127-129, 125]. Oxidation with bromine water yields both disulfides [18, 19, 30] and sulfonic acids [130].

#### e) Behavior toward Halogens in the Presence of Water

In 1936 *Johnson et al.* found [131, 132] that sulfur compounds in general can be converted into sulfonyl halides (19) by halogenation in water.



Bunte salts can be converted similarly into the corresponding sulfonyl halides [133-136]. For analytical purposes [137], bromine water is used instead of chlorine water, so that not only *S*-alkylthiosulfates, but also thiols, disulfides, thio-cyanates, and similar sulfur compounds can be converted into sulfonyl bromides. These react with a cyanide to liberate cyanogen bromide, which can then be determined colorimetrically.

#### f) Reduction of Bunte Salts

The reduction of *S*-alkylthiosulfates with conventional agents, such as sodium amalgam [77], zinc and acid [78, 89, 93, 94, 138], or alkaline sodium arsenite solution [7, 8] leads to thiols. However, this method is of little importance for the preparation of thiols, which can be obtained much more elegantly by cleavage of *S*-alkylthiosulfates with acid.

#### g) Reaction with Cyanides

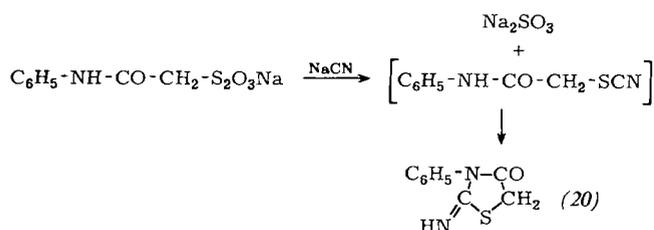
*S*-Alkylthiosulfates are smoothly converted into thiocyanates in the presence of aqueous alkali metal cyanide solution, even at room temperature [76, 139].



Dyes containing *S*-alkylthiosulfate residues can be readily converted into thiocyanates in this manner; these can sometimes undergo ring closure with ad-

- [128] *T. S. Price and D. F. Twiss, J. chem. Soc. (London) 95, 1489 (1909).*  
 [129] *M. Viscontini, K. Adank, N. Merklng, K. Ehrhardt, and P. Karrer, Helv. chim. Acta 36, 835 (1953).*  
 [130] *H. J. Backer, Recueil Trav. chim. Pays-Bas 49, 1048 (1930).*  
 [131] *J. B. Douglass and T. B. Johnson, J. Amer. chem. Soc. 60, 1486 (1938).*  
 [132] *T. B. Johnson and J. M. Sprague, J. Amer. chem. Soc. 58, 1348 (1936).*  
 [133] *C. Ziegler and J. M. Sprague, J. org. Chemistry 16, 621 (1951).*  
 [134] *G. Geiseler and R. Kuschierners, Chem. Ber. 93, 2041 (1960).*  
 [135] *J. M. Sprague, US.-Pat. 2531 367; Chem. Abstr. 45; 3418 (1951).*  
 [136] *G. Dougherty and R. H. Barth, US.-Pat. 2293 971; Chem. Abstr. 37, 889 (1943).*  
 [137] *B. Saville, Chem. and Ind. 1956, 660.*  
 [138] *A. P. Tiselskii, Ukrain. Chim. Ž. 24, 749 (1958); Chem. Abstr. 53, 20039 (1959).*  
 [139] *H. B. Footner and S. Smiles, J. chem. Soc. (London) 1925, 2887.*

adjacent groups [121]. For example, *S*-phenylcarbamoylmethylthiosulfate gives 2-imino-3-phenyl[1,3]thiazolidin-4-one (20), ("3-phenylpseudothiohydantoin"), presumably *via* a linear thiocyanate [30].

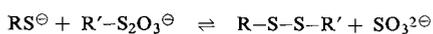


#### h) Reaction with Iodides, Thiocyanates, and Thiourea

Bunte salts react with iodides, and with thiocyanates as pseudohalides, in the acidic range to form disulfides. Thiourea is reported to behave similarly [2].

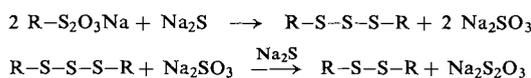
#### i) Reaction with Thiols and Alkali Metal Sulfides

Thiols react with *S*-alkylthiosulfates in alkaline solution to form disulfides [139].



When R and R' are the same, the resulting disulfides are symmetrical. Systems in which R and R' are dissimilar do not yield unsymmetrical disulfides, but give equimolar mixtures of the symmetrical disulfides. However, high yields of unsymmetrical disulfides are reported to be obtained when the reaction is carried out in weakly acidic solutions [140].

The reaction of sulfide ions with Bunte salts in aqueous solution is very complex. Hydrodisulfides together with sodium sulfite [141] as well as disulfides [78] or trisulfides [19] have been suggested as intermediates and/or reaction products. The behavior of dyes containing *S*-alkylthiosulfate residues toward aqueous sulfide solutions is of industrial importance. The reaction leads mainly to water-insoluble aliphatic disulfides, which, unlike aromatic disulfides, are stable toward sulfide ions [121] (cf. Section 3c); the following reactions probably occur:

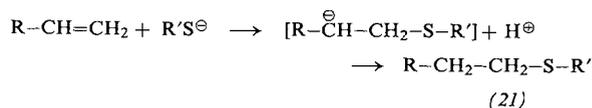
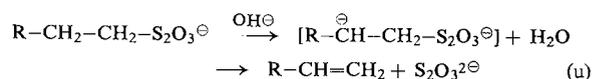


Bunte salts formed by nucleophilic addition of thiosulfate to activated double bonds react differently. The hydroxide ions probably split the Bunte salt into thiosulfate and a compound containing an activated CC double bond. The much more nucleophilic thiolate ion then competes with the thiosulfate ion to form the thioether (21) [5, 142] in accordance with equation (u).

[140] J. M. Swan, *Nature* (London) 180, 643 (1957).

[141] A. Gutmann, *Chem. Ber.* 48, 1162 (1915).

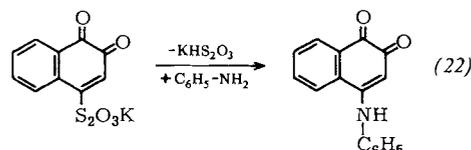
[142] H. Distler, unpublished.



R = e.g., COOR'', CONH<sub>2</sub>, SO<sub>2</sub>OR'', COR'', SO<sub>2</sub>NH<sub>2</sub>, COOH

#### j) Reaction with Amines

*S*-Alkylthiosulfates generally react with amines to form disulfides [2]. An exception was found with Bunte salts of quinones, which undergo nucleophilic substitution with aromatic amines to give the arylaminoquinone, e.g. (22) [143].

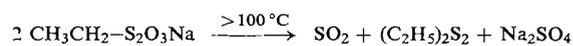


A number of marked deviations from normal behavior are observed in the reaction of Bunte salts with amines. These have been extensively studied, particularly by Swan and Milligan [30, 144].

## 4. Properties and Use of Bunte Salts

### a) General Characteristics

Owing to the presence of the NaS<sub>2</sub>O<sub>3</sub> groups, the *S*-alkylthiosulfates are mostly very readily soluble in water, methanol, ethanol, and other polar solvents. The Bunte salts can be purified by recrystallization from alcohol or alcohol-water mixtures. The salts are occasionally obtained with one molecule of water of crystallization per molecule. Neutral aqueous solutions are frequently decomposed within a few minutes at 100 °C, as can be seen from the turbidity of the solution. Salts of alkali metals or, less commonly, of alkaline earth metals can be used for their isolation. Lead and silver salts are occasionally suitable for the characterization of a compound. It should be noted that *S*-alkylthiosulfates, which crystallize excellently from e.g. alcohol, do not have a true melting point, but rather a sort of sintering point, at which the salt agglomerates like a glass. Dry heating [1, 145] frequently leads to decomposition above 100 °C. According to Bunte [1], sodium *S*-ethylthiosulfate decomposes into diethyl disulfide, sulfur dioxide, and sodium sulfate.

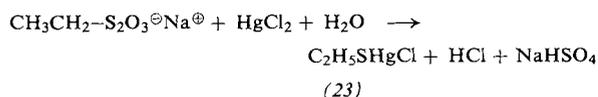


[143] G. Heller, *J. prakt. Chem.* 108, 257 (1924).

[144] B. Milligan and J. M. Swan, *J. chem. Soc. (London)* 1961, 1184.

[145] A. Purgotti, *Gazz. chim. ital.* 20, 25 (1890).

Further characterization is possible by the reaction of the *S*-alkyl-thiosulfates in aqueous alkali with Hg(II) chloride solution, which leads after brief warming to mercaptides such as (23) [11].



### b) Spectra of Bunte Salts

Kunath [146] and Simon [108] found a number of characteristic absorption bands for Bunte salts in the regions 640–660 cm<sup>-1</sup>, 1040–1050 cm<sup>-1</sup>, and 1190 to 1250 cm<sup>-1</sup>. We have been able to confirm these data for a large number of Bunte salts [148]: the bands are generally situated at 648–650 cm<sup>-1</sup>, 1040–1048 cm<sup>-1</sup>, and 1210–1215 cm<sup>-1</sup>.

### c) Biological Action

Sodium *S*-ethylthiosulfate exhibits a striking synergic effect when used with the bacteriostat 2-mercaptobenzothiazole and its derivatives against *Staphylococcus aureus* [149]. A similar synergic effect was observed with sodium *S*-ethylthiosulfate and 2-mercaptobenzothiazole against the tubercle bacillus [150]. Sodium *S*-(3-nitrophenyl)thiosulfate is reported to have a particularly strong preventative and curative action against fowl coccidiosis [23]. According to our own observations, Bunte salts obtained *e.g.* by addition of thiosulfate to aryl vinylsulfonates have a

- [146] D. Kunath, Chem. Ber. 96, 157 (1963).  
 [147] R. Wegler and A. Ballauf, Chem. Ber. 81, 527 (1948).  
 [148] H. Distler, unpublished.  
 [149] G. Bargellini and E. Del Pianto, Atti Accad. naz. Lincei Rend., Cl. Sci. fisiche, mat. nat. 4, 21 (1948); Chem. Abstr. 42, 8867 (1948).  
 [150] E. Del Pianto, Ricerca sci. 20, 83 (1950); Chem. Abstr. 45, 4822 (1951).  
 [151] H. Distler, unpublished.  
 [152] H.U. Schmidlin and W. Zysset, Textilveredlung 1, 20 (1966).

considerable effect on *Aspergillus niger* [151]. Other adducts of thiosulfate with acrylic acid derivatives have a systemic-nematocidal action [151].

### d) Industrial Use

Most patents dealing with the production and the use of Bunte salts are concerned with the textile industry. The "Bunte salt dyes" [121] have attracted particularly wide industrial interest in this field. Bunte salts derived from divinyl sulfone have recently found industrial use in the finishing of textiles, and particularly of cotton [161, 152, 153], in the Stevenseset Super-Crease Process developed by J.P. Stevens (U.S.A.) [162]. The hydrophilic Bunte-salt group gives long-chain hydrophobic compounds a surface activity comparable with that of the sulfation products of fatty alcohols [154, 28, 155–158, 62–64].

*I am grateful to Dr. Lützel for perusal of this article. I should like to thank Dr. Feichtmayr for stimulating discussions, particularly on the reactivity of the thiosulfate anion.*

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 Translated by Express Translation Service, London

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 [154] M. Schmitt and G. Talsky, Chem. Ber. 94, 1352 (1961).  
 [155] A. Kirstahler and W. J. Kaiser, US.-Pat. 2004873 (June 11, 1935); Chem. Abstr. 29, 5124 (1935); German Pat. 636260 (Oct. 15, 1936); Chem. Abstr. 31, 701 (1937).  
 [156] Van R. Gaertner, US.-Pat. 2904582 (Sept. 15, 1959); Chem. Abstr. 54, 2258 (1960).  
 [157] Henkel and Co., Brit. Pat. 417930 (Oct. 16, 1934); Chem. Abstr. 29, 1433 (1935).  
 [158] W. J. Kaiser and A. Kirstahler, German Pat. 639281 (Dec. 2, 1936); Chem. Abstr. 31, 1524 (1937).  
 [159] H. Zollinger, Angew. Chem. 73, 125 (1961); G. D. Gollnisch, Z. Chem. 3, 243 (1963); B. C. M. Dorset, Textile Manufacturer 89, 1057 (1963); H. G. Fröhlich, Z. ges. Textilind. 63, 47 (1961).  
 [160] K. Schimmelschmidt, H. Hoffmann, E. Mundlos, G. Laber, and M. Schorr, Chem. Ber. 96, 38 (1963).  
 [161] Dow Corning Corp., Netherlands Pat. Appl. 6513899 (Oct. 27, 1965).  
 [162] Textile World 1965, 232.

## COMMUNICATIONS

### The Cyclobutenediylum Cation, a Novel Chromophore from Squaric Acid

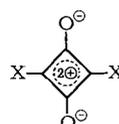
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Dedicated to Professor F. Aisinger on his 60th Birthday

Tertiary amines [1] and azulenes [2], like active pyrroles and phenols [3], condense smoothly with squaric acid (dihydroxycyclobutenedione), giving products that contain the structural element of cyclobutenonolate. Although these compounds are deeply colored it is problematical whether they are to be regarded as cyanine dyes [4]. In agreement with the

conceptions of aromatic character and the results of other authors [5], structure (1) can be assigned to these dyes.

We have introduced, as nucleophilic components, the bases obtained by elimination of HI from 2-methyl-substituted quinolinium, benzothiazolium, and benzoselenazolium iodide. These also yield crystalline, intensely colored, betaine-like dyes (2), which were hitherto unknown. The Fischer base reacts analogously with squaric acid giving the condensation



(1a), X = N, *N*-Dialkylaminophenyl

(1b), X = 1-Azulenyl

(2), X = CH=Z