benzene. After the addition, the stirring was continued for six hours at room temperature. After hydrolysis with saturated ammonium chloride solution, the crude reaction product was refluxed for 3.5 hours with dilute hydrochloric acid in ethanol as the mild hydrolysis described[33] did not effect complete rearrangement to unsaturated ester in our case. Saponification with potassium hydroxide in 95% ethyl alcohol afforded 2.19 g. (63.5%) of crude XVIII. The analytical sample, m.p. 241.8-242.4° dec., was obtained after four recrystallizations from benzene–acetone. A mixture of XVIII with XIX melted at 222-230°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.0; H, 7.0. Found: C, 83.1, 83.1; H, 7.2, 7.1.

Resolution of 1,12-Dimethylbenzo(c)phenanthrene-5-acetic Acid (XIX).[34]—To 2.00 g. of XIX dissolved in hot acetone was added 1.872 g., one equivalent, of *l*-cinchonidine dissolved in hot acetone. Removal of the solvent and trituration of the residue with Skellysolve F (petroleum ether, b.p. 35–40°) afforded a cream-colored solid, m.p. 105–130°, $[\alpha]^{24}D$ −32.5° (c 2 in chloroform). Approximately 600 ml. of warm ether failed to dissolve all the solid. The remaining cinchonidine salt (1 g.) melted at 140–142°, and had $[\alpha]^{24}D$ −153° (c 2 in chloroform). Recrystallization of this material from a large volume of ether at room temperature[35] gave 0.6 g., m.p. 139.8–141.0°, $[\alpha]^{23}D$ −170° (c 2 in chloroform). The analytical sample, recrystallized three times from ether, formed very fine needles in rosettes, m.p. 143.7–145.1° with softening at 140°. The analysis indicated a monohydrate.

Anal. Calcd. for $C_{41}H_{40}O_3N_2\cdot H_2O$: C, 78.6; H, 6.8; N, 4.5. Found: C, 78.5, 78.6; H, 6.9, 7.1; N, 4.2, 4.4.

The original filtrate was concentrated at room temperature and 1.5 g. of white solid which precipitated was separated. The filtrate was concentrated to a viscous oil which formed a cream-colored solid, m.p. 120–124°, $[\alpha]^{23}D$ +43.0° (c 2.45 in chloroform), on trituration with Skellysolve F.

Each of the cinchonidine salts, $[\alpha]D$ −170° and +43.0°,

(33) I. Heilbron, E. R. H. Jones, M. Julia and B. Weedon, *J. Chem. Soc.*, 1823 (1949).

(34) All readings were taken using a Schmidt and Haensch polarimeter in a 2-dcm. tube.

(35) The solutions in these first experiments were not heated as the optical stability of the compound was not known. In later experiments recrystallization from acetone–ether was effective.

was decomposed by the addition of aqueous alcoholic hydrochloric acid. The acid from the (−)-cinchonidine salt gave a rotation of −7.97°, $[\alpha]^{23}D$ −332° (c 1.20 in acetone). Repeated recrystallizations from ether yielded fine crystals, m.p. 207.3–208.4° with slight darkening, $[\alpha]^{25}D$ −362.7 ± 2.5° (c 0.35 in acetone). The acid from the (+)-cinchonidine salt gave a rotation of +6.05°, $[\alpha]^{23}D$ +187° (c 1.62 in acetone). From benzene–acetone some racemic acid crystallized, m.p. 238.5–240.0°. Repeated recrystallizations from ether of the acid obtained from the filtrate yielded fine crystals, m.p. 207.7–208.7° with slight darkening, $[\alpha]^{25}D$ +347.6 ± 3.6° (c 0.29 in acetone). The racemic acid has an m.p. of 243.0–244.4° dec.

Racemization Experiments.—The methyl ester obtained using diazomethane from acid $[\alpha]^{29}D$ −358° had a m.p. of 152–154° and $[\alpha]^{27}D$ −275° (c 0.0340 in chloroform). Rapid distillation of the methyl ester under nitrogen at 0.03 mm. and a bath temperature of 200–210° furnished a sample, m.p. 154–155°, $[\alpha]^{24}D$ −294° (c 0.0332 in chloroform).

The methyl ester ($[\alpha]^{27}D$ −275°, 19.5 mg.) was sealed under 0.05 mm. of nitrogen in a small Pyrex tube. This was immersed completely into a salt-bath kept at 246–250°. After 30 minutes the tube was taken out and cooled rapidly in cold air. The content of the tube was rinsed out thoroughly with chloroform diluted to 5 ml. and polarimeter readings were taken, $[\alpha]^{27}D$ −263° (c 0.039 in $CHCl_3$). The infrared spectrum of the recovered ester was found to be identical with that of the starting material. Crystallization from acetone furnished a sample, m.p. 152–154°.

A similar experiment at 250° for 2 hours resulted in a solution which was too dark to be read in the polarimeter. No crystalline ester could be obtained from this solution.

Similar heating at 294–297° for 30 minutes resulted in considerable darkening of the substance. This product was chromatographed over a short column of activated alumina in benzene–ligroin. After 2 chromatographs a pale yellow solution of the substance was obtained which showed no rotation, but the residue gave an infrared spectrum identical with that of the methyl ester.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Grignard Reaction and Infrared Spectra of Cyclic Sulfites

BY H. HARRY SZMANT AND WILLIAM EMERSON

The reaction of several cyclic sulfites with phenylmagnesium bromide gave phenyl sulfoxide in yields which did not vary greatly with the size of the sulfite ring or with the presence of substituents on the ring. Unlike non-cyclic sulfites, however, the cyclic ones gave some bromohydrins related to the glycol precursors of the sulfites. The infrared spectra of cyclic sulfites are discussed in the light of the known spectra of similar sulfur compounds.

It is well known that the behavior of the carbonyl function in cyclic ketones is greatly affected by the size of the ring.[1] This study was undertaken in the hope to uncover some variations in the behavior of cyclic sulfites as a function of ring size. If cyclic sulfites were to be affected by the size of the ring as are cyclic ketones, then reactivity (toward a Grignard reagent) and some physical properties (such as the stretching frequency of the >S═O bond) would be expected to vary with the relative resonance contributions of structures I–III.

The reaction of Grignard reagents with alkyl or aryl sulfites was reported some time ago as a

method of preparation of sulfoxides,[2] but cyclic
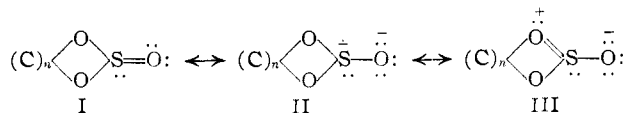
sulfites do not seem to have been studied in this connection. From the results listed in Table I it is evident that the yield of phenyl sulfoxide showed little variation when phenylmagnesium bromide reacts with alkyl, aryl or five- or six-membered cyclic sulfites. Also, in the case of ethylene sulfite the

(1) H. C. Brown, J. H. Brewster and H. Schechter, THIS JOURNAL, 76, 467 (1954).

(2) (a) W. Strecker, *Ber.*, 43, 1131 (1910); (b) L. Bert, *Compt. rend.*, 178, 1826 (1924); (c) H. Gilman, J. Robinson and N. J. Beaber, THIS JOURNAL, 48, 2715 (1926).

yield of phenyl sulfoxide was little influenced by either the ratio of the reagents or the mode of addition.

TABLE I

THE REACTION OF PHENYLMAGNESIUM BROMIDE WITH SULFITES

Sulfite	Condition[a]	Yield, % Phenyl sulfoxide	Bromohydrin
Ethylene	A	59.7	7.0
Ethylene	A	49.8	3.4
Ethylene	B	43.6	15.7
Ethylene	C	46.5	13.0
Ethylene	D	42.4	10.7
Ethylene	E	54.0	22.7
Trimethylene	A	50.8	12.6
Neopentylene[b]	A	55.3	8.5[c]
Phenyl	A	48.7	..[d]
Methyl	A	63.2	..[e]

[a] The following variations in conditions were employed: A = 2:1 ratio of Grignard to sulfite, sulfite added to Grignard; B = 1:1 ratio of reagents, Grignard added to sulfite; C = 2:1 ratio of Grignard added to sulfite; D = 3:1 ratio of Grignard to sulfite, Grignard added to sulfite; E = 1:1 ratio of reagents, sulfite added to Grignard.　[b] This is the sulfite derived from "neopentyl glycol," i.e., 2,2-dimethylpropane-1,3-diol.　[c] There was recovered, in addition to 34.5% of the original glycol, a mixture of the bromohydrin and biphenyl whose analysis was: C, 51.7; H, 7.7; Br, 30.7. This corresponds closely to a mixture of 68% bromohydrin and 32% biphenyl: C, 54.3; H, 6.6; Br, 32.5. The yield of the bromohydrin is estimated on the basis of this mixture.　[d] The phenol was recovered in 87.8% yield.　[e] In a control experiment (see Experimental) 1.8% of methyl bromide was obtained (estimated by precipitation of silver bromide).

Previous investigators of this reaction reported the isolation of the carbon residue of the sulfite as the corresponding alcohol or phenol, but in no case is there an indication that the carbon residue also may have been converted to the halide. An interesting result of this study is the isolation of the bromohydrins related to the glycol residues of the cyclic sulfites. Also of interest is the fact that no dibromo derivatives of the glycol residues were encountered. The latter fact seems to indicate rather strongly that the formation of the carbon–halogen bond takes place when the Grignard reagent reacts with the sulfite while that molecule is still a cyclic structure; the second phase of the reaction involves the opened ring structure and thus there is no longer a carbon–halogen bond being formed. To better appreciate the significance of the formation of the carbon–halogen bond during the reaction of the Grignard reagent with *cyclic* sulfites it should be pointed out that the formation of alkyl halides has been encountered when Grignard reagents reacted with compounds of *tetracovalent* sulfur such as the alkyl sulfates or the alkyl esters of sulfonic acids.[3] Tricovalent sulfur compounds, such as sulfites or sulfinates,[3] were not known to give carbon–halogen bond formation until the present study.

We believe that the above facts can be explained when one considers the probable mechanism of the reaction. Thus, ethylene sulfite and phenylmagnesium bromide, for example, form the complex IV,

(3) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, Chapter XXI.

R = C₆H₅ (IV)
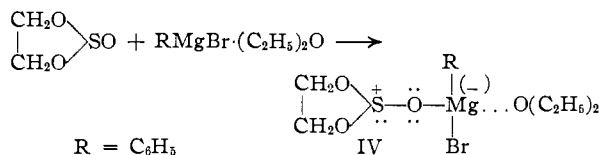
analogous to those postulated in the reaction of Grignard reagents with esters.[4] Subsequently, IV may be cleaved in two possible ways: the first cleavage by attack of another molecule of the Grignard reagent creates a carbon–sulfur bond, and the repetition of this process leads to the formation of phenyl sulfoxide and the magnesium salt of the glycol. These steps are entirely analogous to those
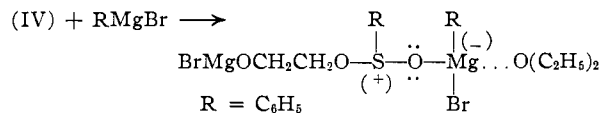

visualized in the reaction of non-cyclic sulfites with Grignard reagents. The second possible mode of cleavage of IV involves the breaking of the carbon–oxygen bond and formation of the carbon–halogen bond by a nucleophilic attack of halide or potential halide ion from the Grignard reagent.

IV + Br⁻...(MgR)⁺ ⟶
BrCH₂CH₂OSOOMgR + RMgBr·(C₂H₅)₂O
R = C₆H₅
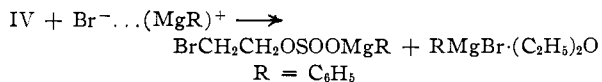
This type of nucleophilic cleavage reaction ordinarily requires a strongly polarized carbon–oxygen bond such as is known to exist in alkyl esters of sulfonic acids or in alkyl sulfates,[5] and in non-cyclic sulfites (and sulfinates) the carbon–oxygen bond is apparently not sufficiently polarized since the sulfur atom holds one less oxygen atom. Also, in non-cyclic sulfites the formation of a complex similar to IV is less favorable because of steric factors and from the consideration of the probable entropy changes, while, on the other hand, the rigidity and greater stability of complex IV could promote the cleavage reaction which creates a new carbon–halogen bond. The resulting product would resemble the intermediate of the Grignard reaction of a non-cyclic sulfite and thus the formation of another carbon–halogen bond would not be expected.

The reaction of 2-bromoethyl phenylmagnesium sulfite with more phenylmagnesium bromide to give phenyl sulfoxide is not unexpected in view

RSOOMgR + RMgBr ⟶ RSOR + BrMg·OMgR
R = C₆H₅
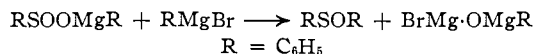
of the fact that the phenylmagnesium salt of benzenesulfinic acid was shown[6] to give phenyl sulfoxide with phenylmagnesium bromide.

RSOOMgR + RMgBr ⟶ RSOR + BrMgOMgR
R = C₆H₅
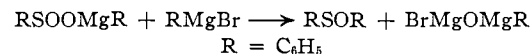
To ascertain the extent of the nucleophilic reaction which takes place in non-cyclic sulfites there was carried out a control experiment with dimethyl sulfite since this non-cyclic sulfite is the most favorable case for the side reaction discussed above.

(4) Reference 3, p. 553.

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 340.

(6) H. Gilman and R. E. Fothergill, THIS JOURNAL, 51, 3501 (1929).

From the amount of methyl bromide produced (and isolated as silver bromide) it is estimated that a maximum of 1.8% of this reaction took place.

Another possible reaction which could account for the formation of the bromohydrins is the decomposition of the bromomagnesium salt of the glycols according to the equation

$$\text{BrMgOCH}_2\text{CH}_2\text{OMgBr} \longrightarrow \text{BrCH}_2\text{CH}_2\text{OMgBr} + \text{MgO}$$
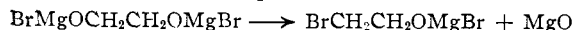
This possibility was eliminated since no ethylene bromohydrin was found in a control experiment using ethylene glycol and an excess of phenylmagnesium bromide.

The infrared spectra of covalent sulfites do not seem to have been reported in the literature. The vibrational spectra of several dialkyl sulfites were, however, studied by the Raman technique[7] and the characteristic sulfur–oxygen stretching frequency was located at about 1200 cm.$^{-1}$. The results of Vogel-Högler with dialkyl sulfites and related compounds are included in Table II for comparison with the results obtained in this study.

TABLE II

THE S–O STRETCHING VIBRATIONS IN SULFITES AND RELATED COMPOUNDS

Sulfite	Absorption, cm.$^{-1}$
Methyl	1213, 1208[a]
Ethyl	1206[a]
Propyl	1202[a]
i-Propyl	1203, 1200[a]
Butyl	1198[a]
Phenyl	1245
Ethylene	1220
Trimethylene	1220
Tetramethylene	1222
Propylene	1222
Pinacol	1225
Neopentylene[b]	1203
α-i-Propylneopentylene[c]	1203
2,5-Dimethylhexane-2,5-diol	1221
Thionyl fluoride	1312[a]
Thionyl chloride	1231[a]
Methyl chlorosulfite	1216[a]
Ethyl chlorosulfite	1215[a]
Propyl chlorosulfite	1212[a]
i-Propyl chlorosulfite	1210[a]
i-Amyl chlorosulfite	1210[a]

[a] Values from ref. 7. [b] Sulfite derived from 2,2-dimethylpropane-1,3-diol. [c] Sulfite derived from 2,2,4-trimethylpentane-1,3-diol.

Replacement of the alkyl groups by phenyl causes a distinct shift to a higher frequency which is in line with the greater electronegativity of the phenyl group. The displacement of the sulfur–oxygen stretching frequency with increasing electronegativity of the groups attached to the sulfur was previously pointed out[8] and is similarly exemplified in the displacement of the Raman frequencies[7] of dialkyl sulfites (1198–1208 cm.$^{-1}$), alkyl chlorosulfites (1210–1216 cm.$^{-1}$), thionyl chloride (1231 cm.$^{-1}$) and thionyl fluoride (1312 cm.$^{-1}$).

The effect of ring size on the stretching frequency

of the carbonyl group in cyclic ketones is very pronounced[9] and while six- and seven-membered ketones have the same frequency as simple dialkyl ketones, the decrease in ring size causes a shift to higher frequencies. This effect is not observed in cyclic sulfites since five-, six- and seven-membered sulfites absorb at practically the same frequency. The non-substituted cyclic sulfites, however, show a small shift to the higher frequencies as compared to the dialkyl sulfites. While the introduction of α-methyl groups in cyclic sulfites causes little if any effect, there seems to be a definite shift toward lower frequencies when the methyl groups are introduced at the β-position. This may be due to the proximity of the hydrogen atoms of the methyl groups to the negative end of the sulfur–oxygen dipole (Fig. 1) and would be analogous to the effect of hydrogen bonding on the stretching frequency of sulfoxides.[8]

In view of the successful correlation of the shifts in the carbonyl frequency as a function of the electronegativity of the groups attached to the carbonyl function,[10] one is tempted to examine the same relationship in the structurally similar sulfur–oxygen compounds. Figure 2 shows the frequencies of several XYSO compounds plotted against the sum of the electronegativities of the groups X and Y using the values suggested by Kagarise.[10] It can be seen that the correlation is not as satisfactory as that found in the corresponding carbonyl compounds. Again, as in the case of dialkyl ketones,[10] the band of the sulfoxides (X,Y = alkyl) is considerably lower than the frequency predicted (using the effective electronegativity values[10] for the methyl group). With the exception of the sulfoxides, the remaining frequencies of the XYSO compounds fall rather well on a smooth curve. The examination of the differences between the carbonyl and the corresponding sulfur–oxygen frequencies when X,Y = F and X,Y = RO, respectively, shows that the difference is approximately twice as large in the carbonyl compounds.[11] Thus, it is evident that the carbonyl stretching frequency is more sensitive to changes in the electronegativity of the substituents and this conclusion is in agreement with that of Moffitt[12] who showed that there is a relatively small variation in bond order in a variety of XYSO and XYSO$_2$ compounds.

The XYSO$_2$ compounds are recognized to have two characteristic bands at approximately 1150 and 1350 cm.$^{-1}$. Of these two frequencies the higher band corresponds most closely to the sulfur–oxygen stretching frequency found in the YXSO compounds.[13] It is of interest to note that the frequencies of sulfuryl chloride, sulfonyl chlorides

(7) R. Vogel-Högler, Acta Phys. Austriaca, 1, 329 (1947); C. A., 42, 6663 (1948).

(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1954, p. 295.

(9) Reference 8, p. 127.

(10) R. E. Kagarise, This Journal, 77, 1377 (1955). It should be pointed out that while the band of dialkyl carbonates (1709 cm.$^{-1}$) agrees with the position predicted by the sum of the electronegativities of two alkoxyl groups (2 × 1.81) the position of the band of dialkyl ketones is approximately 50 cm.$^{-1}$ lower than the predicted frequency.

(11) The difference in the bands of F$_2$CO and (RO)$_2$CO is 1928 − 1709 = 219 cm.$^{-1}$, while F$_2$SO − (RO)$_2$SO = 1312 − 1202 = 110 cm.$^{-1}$.

(12) W. Moffitt, Proc. Roy. Soc. (London), 200A, 409 (1950).

(13) This point is discussed by D. Barnard, J. M. Fabian and H. P. Koch, J. Chem. Soc., 2442 (1949). These authors, however, average the position of the two bands in their own comparisons.

TABLE III

PREPARATION OF SULFITES

Sulfite	Yield, %	Method	B.p. °C.	Mm.	n_D	t, °C.	Sulfur, % Calcd.	Found
Ethylene[a]	75	A	86	35	1.4443	25		
Trimethylene	30	D	88	39	1.4530	20	26.25	25.9
Tetramethylene	10	E	72	9	1.4631	25	23.55	23.5
Pinacol	55	D	..[b]				19.52	19.7
Neopentyl[c]	70	C	95	40	1.4450	25	21.35	21.0
α-i-Propylneopentyl[d]	90	C	100	15	1.4554	26.8	16.67	16.6
2,5-Dimethylhexane-2,5-diol	50	D	..[e]				16.67	16.2
Methyl[f]	51	B	57	56	1.4063	25.3		
i-Propyl	20	A	52	9	1.4126	25.4	19.29	18.95
Phenyl[g]	30	E	149	9	1.5716	24.8		

[a] Prepared according to the method of W. W. Carlson and L. H. Cretcher, THIS JOURNAL, **69**, 1952 (1947). [b] Solid, m.p. 44–45°, crystallized from methanol. [c] Derived from 2,2-dimethylpropane-1,3-diol and prepared according to D. G. Markees and A. Burger, THIS JOURNAL, **71**, 2031 (1949), who reported b.p. 89° (33 mm.) and $n^{25}D$ 1.4465. The product obtained in this study solidified to a solid m.p. 20–20.5°. [d] Derived from 2,2,4-trimethylpentane-1,3-diol. [e] Solid, m.p. 62–63°, crystallized from ligroin. [f] Prepared according to A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, **16** (1943), who reported b.p. 126° (760 mm.) and $n^{20}D$ 1.40929. [g] Prepared according to W. Gerrard, *J. Chem. Soc.*, 218 (1940), who reported b.p. 178° (15 mm.).

and fluorides, and of sulfones fit the curve of the XYSO compounds (Fig. 2) fairly well, if the position of the band near 1350 cm.$^{-1}$ is plotted against the sum of the electronegativity values of X,Y and O (using the effective electronegativity value of the methyl group for all carbon groups attached to sulfur). Unfortunately the frequencies of sulfonic esters and alkyl sulfates do not correlate as satisfactorily.
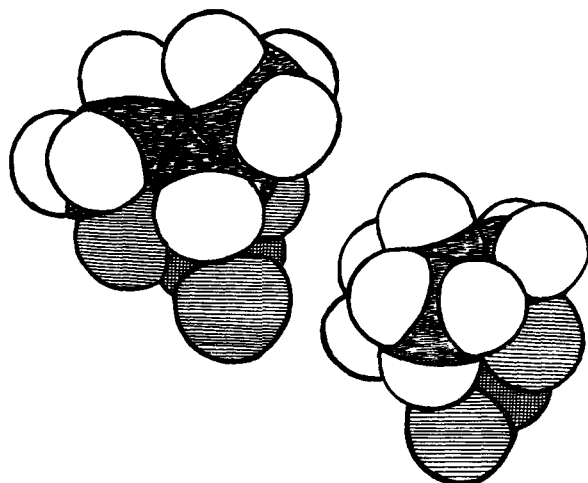

Fig. 1.—Models of α- and β-methyltrimethylene sulfite: the β-methyl group (right) is very near the $>$S⁼⁼O oxygen atom while the α-methyl group (left) cannot approach the oxygen (horizontal lines indicate oxygen, checkered marking indicates sulfur).

Experimental[14]

Preparation of the Sulfites.—The sulfites were prepared from thionyl chloride and the corresponding hydroxy compound by one of the following five methods. (A) The thionyl chloride was added slowly to the hydroxy compound at 35–40° with rapid stirring. The reaction mixture was then heated for 15–30 minutes at 70–75° and fractionated. (B) The above procedure was modified by keeping the reaction temperature at 15° and using a stream of nitrogen to remove the hydrogen chloride as it was formed. (C) An excess of thionyl chloride (one to two molar) was added to the hydroxy compound as rapidly as possible, the mixture was refluxed gently for 1–2 hours, and fractionated. (D)

(14) Analyses by Drs. Weiler and Strauss, Oxford, England.

The thionyl chloride, dissolved in anhydrous carbon tetrachloride, was added slowly to the hydroxy compound stirred with anhydrous carbon tetrachloride at 10–15°. After the addition was completed the mixture was heated to 70° and fractionated. (E) The thionyl chloride, in anhydrous ether, was added slowly to a mixture of the hydroxy compound, pyridine (present in amount sufficient to combine with the theoretical amount of hydrogen chloride produced) and ether or ethyl acetate. The temperature was kept at 0–15° and after complete addition of thionyl chloride the mixture was filtered, to remove pyridine hydrochloride, and the filtrate was fractionated.

The sulfites were purified by fractionation in a semi-micro, all-glass column or by recrystallization. The physical properties and other pertinent data concerned with the sulfites used in this study are summarized in Table III.
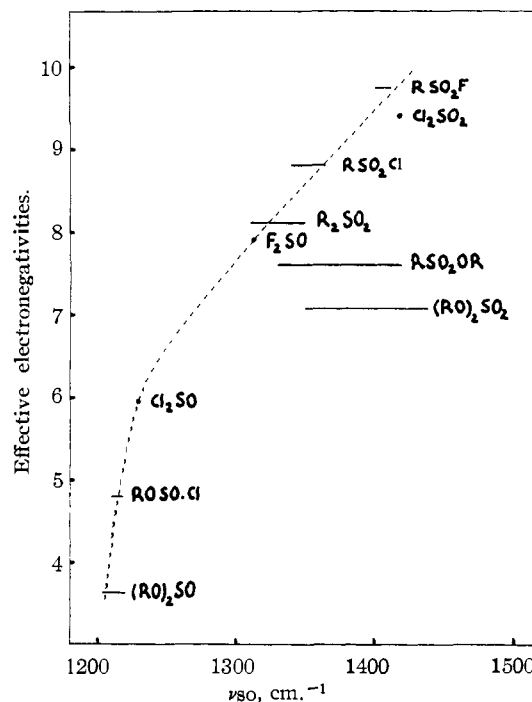

Fig. 2.—Plot of the sum of the electronegativities of substituents *versus* the observed S–O frequencies. (The electronegativity value of CH_3 was used for all R groups.)

Grignard Reaction of the Sulfites.—In a typical experiment the phenylmagnesium bromide was prepared by adding (2 hr.) 64.4 g. (0.41 mole) of bromobenzene, in 350 ml.

of anhydrous ether, to 10.1 g. (0.42 mole) of magnesium turnings. The resulting mixture was refluxed 90 minutes to complete the reaction and to this solution was then added 24.0 g. (0.20 mole) of trimethylene sulfite in 125 ml. of anhydrous ether. The addition was made during 2.5 hours and the reaction mixture then refluxed for 90 minutes. The mixture was hydrolyzed by adding 350 ml. of saturated ammonium chloride solution, the ether layer was separated and the aqueous layer was extracted twice with 200-ml. portions of ether. After drying the combined ethereal solutions over Drierite the solvent was removed and the residue distilled to give the following fractions: (1) b.p. 80–100° (55 mm.), $n^{26}D$ 1.4986; (2) b.p. 90–115° (4 mm.) solidified; (3) residue, solidified. Fraction 1 on redistillation gave 3.5 g. of trimethylene bromohydrin (12.6%), b.p. 75–80° (35 mm.), $n^{25}D$ 1.4834. Fraction 2 was recrystallized from methanol to give 2.0 g. (6.4%) of biphenyl, m.p. 65–68°. The residue was dissolved in benzene and crystallized to give 19.5 g. (50.8%) of phenyl sulfoxide, m.p. 68–69°. The identities of the solids were confirmed by mixture melting points.

Except for changes in ratios of the phenylmagnesium bromide to sulfite, and the order of addition, the Grignard reactions were carried out and worked up as described above. The results are summarized in Table I.

In a blank run to check the yield of biphenyl obtained under the above conditions it was found that 8.3% of biphenyl could be isolated.

To check the formation of methyl bromide during the reaction of phenylmagnesium bromide and methyl sulfite the reaction was carried out under the above conditions using 0.5 mole of phenylmagnesium bromide and 0.154 mole of methyl sulfite. The sulfite dissolved in ether was added to the Grignard reagent while a slow stream of nitrogen swept the gaseous products into two absorption flasks containing 30 cc. of a solution obtained by dissolving 5 g. of potassium hydroxide in 95% ethanol. The absorption flasks were maintained at 0°, and the nitrogen stream was continued during the two-hour reflux period following the completion of the addition of the sulfite. The reaction mixture was worked up in the usual way to give 65% of phenyl sulfoxide. The solution in the absorption flasks was allowed to come to room temperature and then was neutralized by addition of acetic acid, and finally a solution of silver nitrate was added until no further precipitation was observed. The precipitate was filtered, washed with dilute nitric acid, water and dried to give 0.1012 g. of silver bromide (0.00053 mole). Assuming a theoretical yield of 0.308 mole, the actual yield of silver bromide corresponds to 0.6%. Since in three control experiments this analytical procedure detected between 35 and 55% of methyl bromide from a methanolic solution, it is estimated that the maximum yield of methyl bromide is 1.8%.

Infrared Data.—The infrared data were obtained with a Perkin–Elmer model 12-C single beam infrared spectrophotometer using a sodium chloride cell. The spectra were taken in 0.5–2.0 M solutions in carbon tetrachloride in a 0.0025- or 0.0100-cm. cell.

Derivatives of 1-Thia-4,5-diazacyclohepta-2,4,6-triene. II.[1] Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide and the Trifluoromethyl-substituted Dibenzo System Containing Sulfur in Unoxidized Form

By H. Harry Szmant and Ronald L. Lapinski[2]

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Controlled reduction of di-(2-nitro-4-trifluoromethylphenyl) sulfide was successful in the preparation of the 1-thia-4,5-diazacyclohepta-2,4,6-triene system containing sulfur in the unoxidized form. The oxidation of *o,o'*-diamino phenyl sulfone and its trifluoromethyl substitution product by means of phenyliodoso acetate represents an excellent synthetic method for the formation of derivatives of 1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide.

The discovery that under conditions of controlled hydrogenation an *o,o'*-dinitro phenyl sulfone can yield the seven-membered heterocyclic ring 1-thia-4,5-diazacyclohepta-2,4,6-triene, and that this ring system does not tend to decompose with elimination of nitrogen, prompted further study of compounds of this type. Of immediate interest was the synthesis of analogous compounds in which the sulfur atom was present in the unoxidized form in order to ascertain if such a ring system is less stable and tends to produce dibenzothiophene derivatives with the loss of nitrogen. Also, it was desirable to prepare dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene without the trifluoromethyl substituents which were present in the first examples of this series of compounds. The results of these studies are reported in the present publication.

After many unsuccessful attempts to bring about the reduction of di-(2-nitro-4-trifluoromethylphenyl) sulfide with simultaneous ring closure, it was found that the use of zinc in the presence of sodium acetate, and of activated aluminum in an alcoholic medium, gave the cyclic azoxy I and azo II compounds, respectively. The identity of these compounds was proven by the conversion to the previously described cyclic azoxy sulfone III. The cyclic sulfides I and II were found to be stable and heating above their melting points did not induce any loss of nitrogen.

In the search for better synthetic methods yielding the 1-thia-4,5-diazacyclohepta-2,4,6-triene system, the recently described oxidation of anilines by means of phenyliodoso acetate was utilized.[3] The application of this procedure to di-(2-amino-4-trifluoromethylphenyl) sulfone gave an excellent yield of the cyclic azo compound IV, which was

(1) The publication in This Journal., **75**, 6338 (1953), is considered the first in this series.

(2) Taken from the Ph.D. thesis of R. L. L., Duquesne Univ., 1954. Financial aid of the Research Corporation is gratefully acknowledged.

(3) K. H. Pausacker, *J. Chem. Soc.*, 1989 (1953).