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## The Pyrolysis of Sulfites. I. Symmetrical Sulfites

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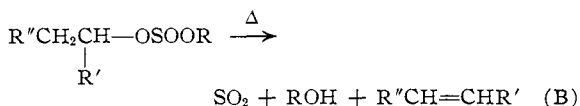
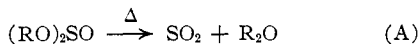
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The pyrolysis of a number of symmetrical sulfite esters of primary and secondary alcohols has been studied. Decomposition to evolve sulfur dioxide begins at temperatures ranging from 130° for  $\alpha$ -methylbenzyl sulfite to 250° for phenethyl sulfite. The principal mode of decomposition is to form olefin and alcohol. Formation of ether was observed only in two cases as a minor product of the reaction. In the case of *n*-amyl sulfite there was some rearrangement to *n*-pentanesulfonate.

In looking for a possible procedure to convert a glycol to an epoxide without inversion of configuration at either carbon atom, we have considered the pyrolysis of the glycol sulfite, which might proceed by a mechanism similar to that proposed for the chlorosulfonates believed to be intermediate in the S<sub>N</sub>i replacement process.<sup>2</sup> Examination of the literature revealed several reports of pyrolysis of sulfites to ethers. For example, ethyl sulfite,<sup>3</sup> benzyl sulfite,<sup>4</sup> phenethyl sulfite<sup>4</sup> and cyclohexyl sulfite<sup>5</sup> were reported to give the corresponding ethers, and 2,3-butylene glycol sulfite the epoxide.<sup>6</sup>

Harispe<sup>7</sup> has reported, however, that 2,4-dimethylphenethyl sulfite decomposed to alcohol and olefins, rather than ether, and Kyrides<sup>8</sup> reported similar observations for cyclohexyl sulfite.

Our investigation of a number of primary and secondary alkyl sulfites of varied structure has indicated (Table II) that the principal mode of decomposition is not to form ether (scheme A) but to produce roughly equimolar portions of alcohol and olefin<sup>4</sup> (scheme B).



(1) E. I. du Pont de Nemours and Co. Fellow, 1952-1953. Abstracted from the Ph.D. dissertation of G. Berti, August, 1953.

(2) See e.g., D. J. Cram, *THIS JOURNAL*, **75**, 332 (1953).

(3) H. Prins, *Ann.*, **223**, 374 (1884).

(4) P. Carre and D. Liberman, *Bull. soc. chim.*, [5] **1**, 1248 (1934); *Compt. rend.*, **198**, 274 (1934).

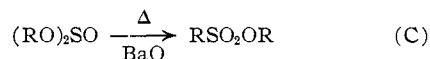
(5) D. Liberman, *Nature*, **160**, 903 (1947).

(6) L. Denivelle, *Compt. rend.*, **206**, 1024 (1939).

(7) G.-V. Harispe, *Ann. chim.*, **6**, 335 (1936).

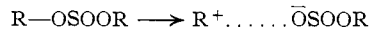
(8) L. P. Kyrides, *THIS JOURNAL*, **66**, 1006 (1944).

In one case (R = *n*-amyl), some rearrangement to *n*-pentane sulfonate was observed.



From 1-methylbutyl and  $\alpha$ -methylphenethyl sulfites, about equal proportions of the two possible olefins were formed. The formation of so much allylbenzene in the latter case, when propenylbenzene would be the more stable isomer, indicates that extensive isomerization of the olefins does not occur during sulfite pyrolysis conditions.

The remarkable difference in the stabilities of benzyl (reactive),  $\alpha$ -methylbenzyl (very reactive), and  $\alpha$ -carbethoxybenzyl (very stable) sulfites suggests that ion-pair character<sup>2</sup> contributes substantially to the transition state for pyrolysis.



Ionization in this sense would be favored by a methyl group but hindered by a carbethoxyl group. The influence of bases on the pyrolysis supports the ionic nature of the reaction, and further evidence for ion-pair character in the transition will be developed in subsequent papers.<sup>9</sup>

### Experimental

**Materials.**—All chemicals used in the preparation of the sulfites were carefully dried. The ether was distilled from sodium, the pyridine from barium oxide. The thionyl chloride used was a commercial product (Matheson Co.); it was redistilled before use when it had a yellow color.

Commercial  $\alpha$ -methylbenzyl, *n*-amyl, 1-methylbutyl and phenethyl alcohols were purified by distillation.

Ethyl mandelate was prepared in 78% yield by the method of Fischer and Speier.<sup>10</sup>

Benzhydrol was prepared according to Wiselogle and Son-

(9) C. C. Price and G. Berti, *THIS JOURNAL*, **76**, 1211ff. (1954).

(10) E. Fischer and A. Speier, *Ber.*, **28**, 3254 (1895).

TABLE I  
 PREPARATION OF SYMMETRICAL SULFITES

Compound, sulfite	Reacn. temp., °C.	Yield <sup>a</sup>	°C.	B.p.	Mm.	<i>n</i> <sub>D</sub> <sup>20</sup>	Sulfur, %	
							Calcd.	Found
α-Methylbenzyl	-80 <sup>b</sup>	(88%) <sup>c</sup>	.....	..	..	1.5440 <sup>d</sup>	...	...
α-Carbethoxybenzyl	-10	82% (93%)	204-208	0.8	..	1.5295 <sup>e</sup>	7.90	7.62
<i>n</i> -Amyl <sup>f</sup>	...	75%	132	15 <sup>g</sup>	..	1.4355	14.43	14.29
1-Methylbutyl	-10	83%	78	1 <sup>h</sup>	..	1.4315	14.43	14.35
Phenethyl	0	86%	205	1 <sup>i</sup>	..	1.5505	...	...
α-Methylphenethyl	-10	57% (83%)	168	0.3	..	1.5367	10.07	10.61

<sup>a</sup> The yields in parentheses are those of crude product, the other ones are for the products purified by distillation. <sup>b</sup> At 10° only 53% of this sulfite is obtained, the rest of the product being mostly α-chloroethylbenzene and styrene. <sup>c</sup> This sulfite could not be distilled even at 0.1 mm., as it decomposed during the distillation. A crude product containing 95% of the sulfite was obtained by stripping off the lower-boiling fractions at 75° and 0.5 mm. <sup>d</sup> Refractive index of the 95% crude product. <sup>e</sup> W. Gerrard, *J. Chem. Soc.*, 85 (1944), reports b.p. 218-221° (2 mm.), *n*<sub>D</sub><sup>20</sup> 1.5272, for the corresponding dextrorotatory compound. <sup>f</sup> This sulfite was prepared following the method of C. M. Suter and H. L. Gerhart, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 112, for the preparation of butyl sulfite. <sup>g</sup> R. Levoillant, *Compt. rend.*, 197, 335 (1933), reports b.p. 134° (13 mm.), *n*<sub>D</sub><sup>20</sup> 1.435. <sup>h</sup> P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, 75, 587 (1927), report for the corresponding dextrorotatory compound b.p. 113-119° at reduced pressure without specifying the pressure. <sup>i</sup> P. Carre and D. Libermann, *Bull. soc. chim.*, [5] 1, 1248 (1934), report b.p. 238-240° (15 mm.).

neborn<sup>11</sup> by reduction of benzophenone with zinc dust and sodium hydroxide.

α-Methylphenethyl alcohol was prepared by the following method. Phenylacetone (Eastman Kodak Co., Practical grade) was distilled twice, collecting the fraction boiling at 210-212°. In a 2-l., three-necked flask, 26 g. (0.7 mole) of lithium aluminum hydride was stirred for 15 minutes with 300 ml. of dry ether, then 268 g. (2 moles) of purified phenylacetone was added from a dropping funnel at such a rate as to keep a slow reflux. This took 90 minutes, the stirring was continued for 15 more minutes, then water was added slowly from the funnel until all reaction subsided. The contents of the flask were poured into an excess of water, enough dilute sulfuric acid was added to dissolve all the solid and the ether layer was washed with sodium carbonate solution and dried over sodium sulfate. After elimination of the ether and distillation, 253 g. (93%) of α-methylphenethyl alcohol was obtained, b.p. 217-218°, *n*<sub>D</sub><sup>20</sup> 1.5210 (lit. b.p. 219-221°, <sup>12</sup> 214.5-215.5<sup>13</sup>).

**General Procedure for the Preparation of Symmetrical Sulfites.**—The reactants were used in the ratio of 1 mole of the alcohol to 0.5 mole of thionyl chloride and 1.1-1.2 moles of pyridine. The following procedure was generally employed, unless otherwise stated. The reaction was run in a three-necked round-bottomed flask of appropriate size, provided with mercury-sealed stirrer, dropping funnel and calcium chloride tubes on the third neck and on top of the dropping funnel. The solution of the alcohol and the pyridine in ether was placed in the flask and thionyl chloride solution in ether was added dropwise with stirring. The temperature was controlled with an appropriate bath as shown in Table I. After the addition of thionyl chloride was completed, stirring was continued for 30 minutes to one hour, then the precipitated pyridine hydrochloride was filtered off and the filtrate washed with 0.1 *N* hydrochloric acid, with water and with 2% sodium bicarbonate solution, dried over magnesium sulfate and the solvent was eliminated *in vacuo*. When stable, the sulfites were purified by vacuum distillation.

**Analysis of Organic Sulfites.**—Iodometric methods, based on the alkaline hydrolysis of the sulfite esters to inorganic sulfite, followed by neutralization and titration with standard iodine solution, did not prove satisfactory, as low results were obtained, due to loss of sulfur dioxide by evaporation or oxidation. On the other hand, the following gravimetric procedure was found to give very good results (within 1% error). In a 200-ml. beaker, a weighed sample of 0.2 to 0.3 g. of sulfite ester was dissolved in 10 ml. of methanol, and about 1 g. of solid potassium hydroxide was added. The mixture was heated on a hot-plate until all the potassium hydroxide had dissolved, then three portions of 2 ml. of water were added at 5-minute intervals. Another 50 ml. of water was then added and the solution was kept

boiling for 30 minutes. Hydrogen peroxide (2 ml. of 30% solution) was added and, after another 10 minutes of boiling, concentrated hydrochloric acid was used to acidify slightly and the sulfate ion was precipitated with barium chloride. The amount of barium sulfate formed was determined by the usual gravimetric method.

**Attempts to Prepare Benzhydryl Sulfite.**—(I) Benzhydryl (61 g., 1/3 mole) and 26.3 g. (1/3 mole) of pyridine were dissolved in 300 ml. of ether, the solution was cooled in an acetone-Dry Ice-bath and 19.8 g. (1/6 mole) of thionyl chloride was added with stirring in 90 minutes. Stirring was continued until the temperature reached 0°, then the mixture was filtered. The residue (61 g.) consisted of impure pyridine hydrochloride. A Volhard titration showed that it contained 0.233 mole of pyridine hydrochloride (theor. 0.333 mole). It was treated with water; the insoluble material was mostly unchanged benzhydryl. The ether solution was washed with water and partly evaporated; some more benzhydryl separated. After complete elimination of the solvent, the residue was redissolved in benzene and an excess of petroleum ether was added. Crystals, m.p. 105-106°, separated (18 g., benzhydryl ether).

(II) The reaction was repeated with 36.8 g. (0.2 mole) of benzhydryl and 15.8 g. (0.2 mole) of pyridine in 150 ml. of ether and 11.9 g. (0.1 mole) of thionyl chloride in 100 ml. of ether, keeping the temperature between -10° and -3° and completing the addition in 2 hours. Precipitate: 21 g., treatment of which with water left 8 g. of impure benzhydryl undissolved. The water layer, on Volhard titration, was found to contain 0.112 mole of chloride. Ether solution: after washing with water and eliminating the ether, 31 g. of residue was left. The benzhydryl chloride was determined in it by dissolving a sample in acetone and titrating with standard aqueous silver nitrate and potassium thiocyanate, according to Volhard; 0.095 mole (47%) of benzhydryl chloride was so found to be present in the reaction mixture.

The residue from the ether solution was dissolved in a little methanol, giving a solid residue (8 g.), which on recrystallization from petroleum ether melted at 108-110° (benzhydryl ether).<sup>14</sup> No evidence at all for the formation of benzhydryl sulfite was found.

**Pyrolysis of Symmetrical Sulfites. Determination of the Pyrolysis Temperature.**—Two methods were used for the determination of the decomposition temperatures of sulfites. (a) A small flask connected to a manometer was used. The temperature was slowly raised and the pressure

(14) The methanolic mother liquor, after being left at room temperature for 20 days, was evaporated. The residue distilled almost completely at 142° (14 mm.) and had *n*<sub>D</sub><sup>20</sup> 1.5085. A sodium fusion showed only a trace of halogen, so that it was deduced that the benzhydryl chloride had been solvolysed by the methanol, giving benzhydryl methyl ether, for which E. Bergmann and J. Hervey, *Ber.*, 62, 915 (1929), report b.p. 147° (17 mm.). The tendency of benzhydryl chloride to solvolysis is well known (e.g., A. M. Ward, *J. Chem. Soc.*, 2289 (1927), obtained benzhydryl ethyl ether on short heating of benzhydryl chloride with ethanol).

(11) F. Y. Wiselogle and H. Sonneborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 90.

(12) G. Austerweil and G. Cochin, *Compt. rend.*, 150, 1603 (1910).

(13) G. Errera, *Gazz. chim. ital.*, 16, 315 (1886).

recorded at 5° intervals. The beginning of the decomposition was shown by a sharp increase in pressure. (b) Nitrogen was bubbled through the sulfite, while heating it slowly, and the outgoing gases were passed through an aqueous solution of barium chloride, containing some hydrogen peroxide. The start of the decomposition was indicated by the formation of a turbidity due to the precipitation of barium sulfate. The two methods gave very similar results.

**Pyrolysis of  $\alpha$ -Methylbenzyl Sulfite.**—Decomposition of this sulfite started at 130–135°, when the compound was heated alone, at 110–115° if two drops of dimethylaniline was added.

(I) Crude  $\alpha$ -methylbenzyl sulfite (5 g., 93% purity) was heated in a 10-ml. distilling flask in a stream of nitrogen. The temperature was raised from 150° to 170° in 20 minutes. At the end of this time the evolution of sulfur dioxide subsided. Some distillate consisting of two immiscible layers had gone over. On washing with water, one of the layers disappeared and the remaining organic layer weighed 2.3 g., had  $n_D^{20}$  1.5450 (styrene 1.5462) and boiled completely at 144–146°.

The undistilled residue in the flask weighed 1.5 g.,  $n_D^{20}$  1.5290. It was mainly  $\alpha$ -methylbenzyl alcohol ( $n_D^{20}$  1.5269) as it all boiled at 103–105° (12 mm.), except for 0.2 g. of undistillable polymeric material. No evidence was found for the formation of  $\alpha$ -methylbenzyl ether.

(II) A 50-ml. distilling flask, containing 16 g. of  $\alpha$ -methylbenzyl sulfite and 2 g. of barium oxide, was connected to a receiver kept at room temperature and to a second one kept in Dry Ice-acetone. The system was evacuated to 1 mm. and the flask heated to 150° until all liquid had distilled. In the receiver at room temperature, 7.31 g. of liquid, b.p. 100–110°,  $n_D^{20}$  1.5305, had collected ( $\alpha$ -methylbenzyl alcohol); in the second one, 4.55 g. of liquid,  $n_D^{20}$  1.5420 (after elimination of the sulfur dioxide), which on redistillation yielded a main fraction, b.p. 144–146° (styrene). Again, no evidence was found for the formation of  $\alpha$ -methylbenzyl ether.

**Pyrolysis of  $\alpha$ -Carbethoxybenzyl Sulfite.**—A 20-g. sample of  $\alpha$ -carbethoxybenzyl sulfite was heated in a 50-ml. distillation flask, in a nitrogen stream, at 240–260°. The side-arm of the flask was connected to a receiver kept at room temperature, while the gaseous products of the pyrolysis were bubbled through a carbonate-free solution of sodium hydroxide. After 1 hour all evolution of sulfur dioxide had ceased and about 2 g. of distillate had collected in the receiver. On redistillation, after a few drops of forerun at 80–85° (probably ethanol), most of this liquid distilled at 180°, had a strong smell of bitter almonds and gave a semicarbazone, m.p. 218–220° (benzaldehyde).

The sodium hydroxide solution was treated with 30% hydrogen peroxide to oxidize the sodium sulfite to sodium sulfate and then it was acidified with hydrochloric acid; some gas was formed, which gave a precipitate with barium hydroxide solution (carbon dioxide).

The residue in the pyrolysis flask smelled strongly of phenylacetic acid. It was dissolved in ether, washed with sodium bicarbonate (only a trace of precipitate was observed on acidifying this solution) and was dried over magnesium sulfate. The residue after elimination of the ether was distilled under reduced pressure.

Fraction	B.p., °C.	Press., mm.	Weight, g.
I	64–78	0.5	2
II	78	.5	0.4
III	78–160	.5	1
IV	160–168	.4	5
V	168–245	.3	3

A dark gummy residue (4 g.) was left in the flask. All fractions and the residue were subjected to hydrolysis with ethanolic potassium hydroxide, and all gave liquid acids, which did not solidify even after months of storage at –10°. Attempts to obtain solid anilides were unsuccessful too, except in the case of the saponification product of fraction I. After the usual treatment with thionyl chloride and aniline, this gave an oily product, but with a mixture of benzene and petroleum ether some crystals were obtained. Two crystallizations from aqueous methanol gave 0.1 g. of product, m.p. 116–118° (mixed melting point with phenylacetanilide, 116–118°).

The residue of a similar pyrolysis was saponified with so-

dium ethoxide, according to the method of Wislicenus<sup>15</sup> for the saponification of diethyl phenylmalonate to sodium phenylmalonate. The saponification mixture was acidified fractionally, but all fractions were liquids. Only the first fraction, on treatment with benzene and recrystallization from petroleum ether, gave a small amount of needles, m.p. 118–120° (mixed m.p. with benzoic acid, 119–121°). Attempts to prepare solid anilides and anilides from the other fractions, according to standard methods,<sup>16</sup> failed again.

Other attempts were made to pyrolyze  $\alpha$ -carbethoxybenzyl sulfite at reduced pressure, by passing its vapors through a hot tube, or dropping the liquid through a heated column packed with glass helices, but no better results were obtained. In all the experiments mentioned above no evidence was found for the formation of di- $\alpha$ -carbethoxybenzyl ether. This compound has been described in the literature<sup>17</sup> as an undistillable viscous liquid; the corresponding acid is a solid melting above 300°, of very low solubility in most organic solvents, so that it should not have been difficult to identify it in the pyrolysis products.

**Pyrolysis of  $n$ -Amyl Sulfite.**—(I) When 20 g. of this sulfite was heated under reflux with an air condenser and the volatile products were collected in a Dry Ice-acetone trap it was found that at the end of three hours only a few drops of liquid had distilled into the receiver. The residue in the flask had  $n_D^{20}$  1.4350 and still contained 96% of  $n$ -amyl sulfite.

(II)  $n$ -Amyl sulfite (20 g.) and 2 g. of barium oxide were heated in a distillation flask connected to a condenser, with a receiver in Dry Ice. Decomposition and evolution of sulfur dioxide started at 200°, but after 2 hours at 225° very little had distilled. After the temperature had been raised to 250–255° for 90 minutes, only a solid residue was left in the flask (4.8 g.). The distillate weighed 16.4 g. and it was redistilled from a steam-bath into a flask cooled in ice-water to separate the pentene and eliminate the sulfur dioxide. Distillate: 3.1 g.,  $n_D^{20}$  1.3750 (mostly pentene). Residue: 9.6 g.,  $n_D^{20}$  1.4180 (it contained only a trace of sulfite). This residue was fractionated at ordinary pressure.

Fraction	B.p., °C.	$n_D^{20}$	Weight, g.	Main product
I	125–135	1.4126	0.8	
II	135–140	1.4100	3.5	$n$ -Amyl alcohol
III	140–147	1.4106	1.0	
IV	147–159	1.4125	1.1	
V	159–190	1.4170	0.8	$n$ -Amyl ether
VI	190–194	1.4252	0.6	

About 1.5 g. of residue with a pleasant aromatic odor was left in the flask,  $n_D^{20}$  1.4460, which boiled between 80 and 170° (10 mm.), evidently a mixture of polymers.

The solid residue in the pyrolysis flask was extracted with ether. Evaporation of the ether left 1.1 g. of yellow oil  $n_D^{20}$  1.4628. The remaining solid was heated with dilute sodium hydroxide solution, and carbon dioxide was passed through the suspension which then was filtered. The filtrate, on evaporation to dryness, left a white residue, which was extracted with boiling 95% ethanol. After elimination of the ethanol, the residue, 1 g. of white crystals, was purified by crystallization from absolute ethanol, yielding shining leaflets which charred without melting (the residue of the ignition gave a positive test for sulfate with barium chloride and hydrochloric acid). No sulfur dioxide was evolved on acidification of this salt. The phenylhydrazine salt was prepared by the method of Latimer and Bost<sup>18</sup> and melted, after crystallization from ethanol and ether, at 106–108° (lit. m.p. of phenylhydrazonium pentanesulfonate, 108°<sup>18</sup>).

(III) When 10 g. of the sulfite was heated for 3 hours at 270° with 0.5 g. of potassium hydroxide, only very little decomposition took place (distillate 0.8 g.). The residue had  $n_D^{20}$  1.4320. The potassium hydroxide was transformed into a mixture of potassium sulfite and potassium pentanesulfonate.

(IV) Heating  $n$ -amyl sulfite with dimethylaniline in exactly the same conditions as used by Voss and Blanke<sup>19</sup> to

(15) W. Wislicenus, *Ber.*, **27**, 1093 (1894).

(16) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

(17) M. Godchot, *Compt. rend.*, **177**, 1225 (1923).

(18) P. H. Latimer and R. W. Bost, *This Journal*, **59**, 2500 (1937).

(19) W. Voss and E. Blanke, *Ann.*, **465**, 258 (1931).

transform methyl sulfite into trimethylanilinium methane-sulfonate, did not result in the formation of any pentyldimethylanilinium pentanesulfonate.

**Pyrolysis of 1-Methylbutyl Sulfite.**—(I) In a 50-ml. flask with a 20-cm. air condenser and a distillation head on the top, connected to a water-cooled condenser leading to a receiver cooled in a water-ice-bath, 10 g. of 1-methylbutyl sulfite was refluxed for one hour. At the end of this time about 3 g. of residue ( $n_{20}^D$  1.4260, mostly 1-methylbutyl sulfite) remained in the flask. The distillate was redistilled from a steam-bath into a collector kept at 0°. The volatile fraction all went over at 30–35°, 1.8 g.,  $n_{20}^D$  1.3760 (pentene), while the residue, 2.6 g., had  $n_{20}^D$  1.4042 (1-methylbutanol).

(II) In the same apparatus, a mixture of 10.7 g. of the sulfite and 1.8 g. of barium oxide was heated, while the receiver was kept in a Dry Ice-acetone-bath. The flask was kept at 210–240° for 3 hours before all liquid had distilled, leaving a solid residue of 2.7 g. The distillate weighed 7.7 g. after being kept at 0° for 2 hours to allow the sulfur dioxide to evaporate. The olefinic products were separated from the higher-boiling material as described in I. Distillate: 2.3 g.,  $n_{20}^D$  1.3760 (pentenes); residue: 4.1 g.,  $n_{20}^D$  1.4050, b.p. 110–120° (1-methylbutanol).

The solid residue in the pyrolysis flask yielded 0.2 g. of a sodium salt, by the same method as described for the corresponding residue of the pyrolysis of *n*-amyl sulfite.

In both cases no evidence was found for the formation of 1-methylbutyl ether. The amounts of pentenes given above may have been low due to losses caused by the low boiling points of the pentenes. The refractive index of the hydrocarbon fractions indicated about a 50/50 ratio of 1-pentene ( $n_{20}^D$  1.3711) and 2-pentene ( $n_{20}^D$  1.3808), but this might again not be entirely accurate as more of the more volatile 1-pentene might have been lost.

**Pyrolysis of Phenethyl Sulfite.**—On heating phenethyl sulfite alone a small amount of sulfur dioxide started evolving at 250° but a sharp increase in pressure was observed only at 270°. When some alumina was present, strong decomposition was observed at 150°. In the presence of pyridine, the mixture turned dark at 170° but strong evolution of sulfur dioxide started only around 220°.

(I) The pyrolysis was performed in a 100-ml. distilling flask connected to a receiver at room temperature and to a second one kept in a Dry Ice-acetone-bath; 27 g. of the sulfite was used. A pressure of 120 mm. was maintained in the system and the sulfite was heated at 295° until only a small amount (1.5 g.) of resinous material remained in the flask. The heating was discontinued and the pressure reduced to 0.2 mm. for one hour, in order to transfer all the styrene into the Dry Ice-cooled flask: 6.6 g. of material collected in this receiver,  $n_{20}^D$  1.5315, which gave the following fractions on distillation at ordinary pressure.

Fraction	B.p., °C.	$n_{20}^D$	Weight, g.
I	130–137	1.5208	2
II	137–142	1.5282	2
III	142–146	1.5380	2

A small glassy residue (probably polystyrene) remained in the distillation flask. The three fractions consist of styrene contaminated with a substance of lower boiling point and refractive index, probably ethylbenzene (b.p. 136°,  $n_{20}^D$  1.4959).

The products of the pyrolysis that had collected in the receiver at room temperature weighed 14.2 g. and gave a positive test for organic sulfite;  $n_{20}^D$  1.5450. This mixture was fractionated at 1 mm.

Fract.	B.p., °C.	$n_{20}^D$	Wt., g.	
IV	76–100	1.5332	2.5	Phenethyl alc.
V	100–153	1.5503	1.2	
VI	153–190	1.5496	6	

Fraction VI was shaken with 25 ml. of 10% methanolic potassium hydroxide to saponify the sulfite still present, the solution was diluted with water and extracted with ether. After elimination of the ether, the residue was refractionated at 0.8 mm.

Fract.	B.p., °C.	$n_{20}^D$	Wt. g.	
VIa	72–75	1.5328	2	Phenethyl alc.
VIb	138–150	1.5450	2	Phenethyl eth.

Comparison of the infrared spectrum of fraction VIb with that of an authentic sample of phenethyl ether, b.p. 154° (3 mm.),  $n_{20}^D$  1.5476, prepared according to Senderens,<sup>20</sup> showed almost complete similarity.

(II) When 15 g. of phenethyl sulfite and 5 g. of alumina were heated at a pressure of 24 mm. for 30 minutes at 195° most of the sulfite decomposed, as a test on the residue showed, but only 4 g. of liquid distilled, which did not contain any styrene and had  $n_{20}^D$  1.5408. The residue in the flask was extracted with ether, 7 g. of extract,  $n_{20}^D$  1.5504, being obtained. Vacuum distillation of this gave only 2.5 g. of phenethyl alcohol, while the residue was an undistillable resin (polystyrene?).

**Pyrolysis of  $\alpha$ -Methylphenethyl Sulfite.**—The decomposition temperature of this sulfite was found to be 235°. An 11-g. sample of the sulfite was heated in a 25-ml. distilling flask in a nitrogen stream. The temperature was kept at 240° until most of the liquid had distilled, only 0.4 g. of dark material remaining in the flask. A sodium hydroxide solution had absorbed 95% of the calculated amount of sulfur dioxide. The distillate weighed 9.0 g. (calcd. 8.7 g.),  $n_{20}^D$  1.5260.

*Anal.* Hydroxyl determination by the acetic anhydride-pyridine method of Freed and Wynne<sup>21</sup> gave 42% of alcohol (calculated as  $\alpha$ -methylphenethyl alcohol).

Olefin titration with bromine according to the method of Uhrig and Levin<sup>22</sup> gave 60% of olefin (calculated as  $C_9H_{10}$ ).

A 4-g. sample of the crude product was distilled from a 10-ml. claisen flask, provided with a 10-cm. Vigreux column, and the hydrocarbon fraction, b.p. 95–105° (100 mm.),  $n_{20}^D$  1.5280, was collected. After redistillation from metallic sodium the  $n_{20}^D$  was 1.5282, corresponding roughly to 45% of propenylbenzene ( $n_{20}^D$  1.5492) and 55% of allylbenzene ( $n_{20}^D$  1.5110). No  $\alpha$ -methylphenethyl ether was found among the products.

TABLE II  
RESULTS OF THE PYROLYSIS OF SYMMETRICAL SULFIDES

Sulfite	Dec. temp., °C.	Products			Observations
		Olefin <sup>b</sup>	Alcohol <sup>b</sup>	Ether <sup>c</sup>	
$\alpha$ -Methylbenzyl	130	128	70	0	
$\alpha$ -Methylbenzyl	110	80	109	0	With BaO
<i>n</i> -Amyl	200	49	67	10	With BaO
1-Methylbutyl	240	82	92	0	
1-Methylbutyl	200	70	98	0	With BaO
Phenethyl	250	50	50	25	
$\alpha$ -Methylphenethyl	235	125	75	0	

<sup>a</sup> The approximate temperatures at which decomposition starts are given. <sup>b</sup> The % of olefin and alcohol, as compared to the amount calculated from the equation  $R-CH_2-CHR'-O-SO_2-O-R'' \rightarrow R-CH=CH-R' + R''-OH + SO_2$  are given. <sup>c</sup> The % of ether with respect to that calculated from the equation  $R_2SO_3 \rightarrow R_2O + SO_2$  is given.

#### NOTRE DAME, INDIANA

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