[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Pyrolysis of Sulfites. II. Glycol Sulfites[1]

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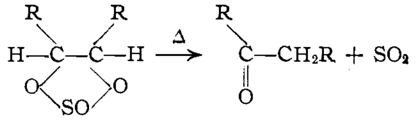
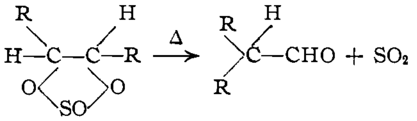
Pyrolysis of the diastereoisomeric forms of the cyclic sulfites of hydrobenzoin and 1,2-cyclohexanediol proceeded smoothly with evolution of sulfur dioxide at 250–300°. In the *cis*-isomers, a hydrogen atom migrated to produce desoxybenzoin and cyclohexanone, respectively. The *trans* isomers gave excellent yields of diphenylacetaldehyde and cyclopentaldehyde, respectively.

The report by Denivelle[3] that pyrolysis of 2,3-butylene glycol sulfite gave, in part, 2,3-butylene oxide, led to an investigation of the possibility that this reaction might give isomeric epoxides from diastereoisomeric glycol sulfites. In the cases chosen for study, however, hydrobenzoin and 1,2-cyclohexanediol, the pyrolysis of the cyclic sulfites proceeded smoothly and in excellent yield[3a] to produce ketone from the two *cis*-isomers (reaction A), aldehyde from the *trans* (reaction B).



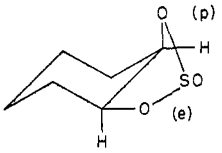
(A)



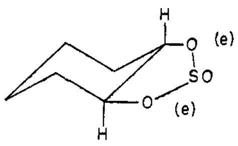
(B)

IA and IB, R = R = C_6H_5
IIA and IIB, R + R = $(CH_2)_4$

In the case of the cyclohexanediols, we may represent the two isomers as follows



IIA

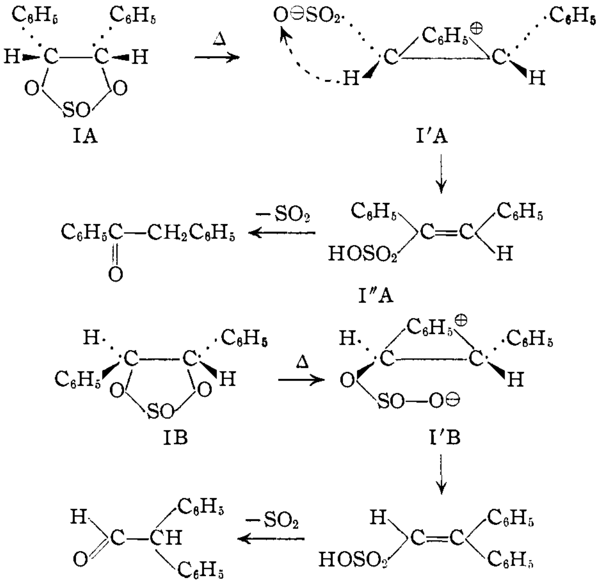


IIB

For compound IIA, ionization would undoubtedly be preferred at the polar oxygen bond rather than at the equatorial oxygen bond. Migration of the *trans*-hydrogen and loss of sulfur dioxide would form the observed product, cyclohexanone. For the most probable conformation of the *trans* isomer IIB ionization at either oxygen, followed by migration of the *trans*-methylene group and loss of sulfur dioxide would form the observed product, cyclopentaldehyde.

In the case of the hydrobenzoin sulfites IA and IB the explanation was not quite so obvious, since in this instance in each compound the phenyl group could participate equally well in forming a cyclic phenonium ion.

We ascribe the different course of the reaction in the case of the isomeric hydrobenzoin sulfites to the fact that the bridged-phenonium zwitterion I'A from the *cis*-sulfite has the sulfinite ion *trans* to the phenyl-activated β-hydrogen and is therefore forced to stabilize by abstraction of the α-hydrogen (quasi-five-membered ring). In the bridged phenonium zwitterion from the *trans*-sulfite I'B, the activated β-hydrogen and the sulfinite are *cis*, permitting easy migration of this proton to form I''B (quasi-six-membered ring).



IA I'A I''A IB I'B I''B

Experimental

Materials.—All chemicals were carefully dried before use. *meso*-**Hydrobenzoin** was prepared by reduction of benzil with lithium aluminum hydride. Benzil (70 g.) was dissolved in 750 ml. of dry ether and the solution was added with stirring during two hours to a slurry of 10 g. of lithium aluminum hydride in 200 ml. of ice-cooled ether. The stirring was continued for 30 minutes at room temperature. The contents of the flask were poured into 1 liter of ice and water, containing 40 g. of sulfuric acid; an additional 500 ml. of ether was added, but some organic material still remained undissolved. This was filtered off, yielding 20 g. of product, m.p. 115–130°. The ether layer, on evaporation, gave 52 g. of material, m.p. 110–130°. The two products were crystallized from ethanol, giving 42 g. of *meso*-hydrobenzoin, m.p. 135–136°. From the mother liquor, rather laborious crystallizations from aqueous ethanol and from benzene gave another 20 g. of *meso*-hydrobenzoin (total yield 87%).[4]

dl-**Hydrobenzoin** was prepared by the method of Breuer and Zincke,[5] based on the bromination of *trans*-stilbene to the *erythro*-bromide, followed by reaction with potassium acetate and acetic anhydride to give the diacetyl derivative of *dl*-hydrobenzoin and saponification of the latter. While

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[1] Presented at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

[2] E. I. du Pont de Nemours and Co. Fellow, 1952–1953. Abstracted from the Ph.D. dissertation of G. Berti, August, 1953.

[3] L. Denivelle, *Compt. rend.*, **208**, 1024 (1939).

[3a] In the case of cyclopentaldehyde, the product quickly polymerized to a mixture of crystalline and liquid polymers.

[4] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949), used lithium aluminum hydride for the reduction of benzil to *meso*-hydrobenzoin, but do not give experimental details.

[5] A. Breuer and T. Zincke, *Ann.*, **198**, 154 (1879).

the bromination of *trans*-stilbene gave a fairly good yield (82%), the next steps were found very unsatisfactory. Not even the low yield (33%) given by Breuer and Zincke could be duplicated. The hydrobenzoin obtained always was a mixture of the *dl*- and *meso*-forms, which are rather difficult to separate. Perhaps the most satisfactory, although very slow, way to perform this separation was found to be the following. The mixture was dissolved completely in cold ether and left to crystallize slowly in the dark in a flask tightly plugged with glass wool. In this way rather large crystals of the stereoisomers were formed. They were easily recognizable from each other, as the *meso* form separates in diamond-shaped crystals, and the *d*- and *l*-forms in long prisms with rounded edges.[6] The individual crystals were separated mechanically and the prisms were crystallized from aqueous ethanol, yielding pure *dl*-hydrobenzoin, m.p. 118–120°, in an over-all yield of 10 to 15%.

cis-1,2-**Cyclohexanediol** was prepared by permanganate oxidation of cyclohexene, both by the method of Markovnikov[7] and of Clarke and Owen.[8] Both methods gave yields of only 20–25% of *cis*-1,2-cyclohexanediol, m.p. 98°.

trans-1,2-**Cyclohexanediol** was obtained by a modification of the method of Roebuck and Adkins.[9] The long extraction of the diol with large volumes of ethyl acetate was avoided in the following way. The alkaline solution formed by adding sodium hydroxide to the mixture obtained in the oxidation of 125 g. of cyclohexene with performic acid was saturated with carbon dioxide, and the bulky precipitate was filtered off and washed with 100 ml. of water to yield 102 g. of product, m.p. 95–100°. The filtrate was concentrated under reduced pressure to a semi-solid mass, which was extracted twice with 200 ml. of boiling benzene. Evaporation of the benzene gave 38 g. of less pure material, m.p. 85–95°. Recrystallization from benzene was found to be preferable to vacuum distillation for the purification; 128 g. of pure *trans*-1,2-cyclohexanediol, m.p. 102–104°, was so obtained (73% yield).

Preparation of Cyclic Sulfites. *meso*-**Hydrobenzoin Sulfite.**—To 20 g. of *meso*-hydrobenzoin and 14.8 g. of pyridine in 500 ml. of ether, 11.1 g. of thionyl chloride in 40 ml. of ether was added in 40 minutes, keeping the temperature close to 0°. The slurry was filtered, 29.5 g. of residue being obtained (pyridine hydrochloride, calcd. 21.4 g.). Extraction of this residue with water left 8.1 g. of organic material undissolved. The ether solution was washed with water and dried over magnesium sulfate; evaporation of the ether left a white residue, weighing 14.5 g. The combined products were crystallized from a mixture of benzene and Skellysolve B, then from absolute ethanol, yielding 20 g. (83%) of *meso*-hydrobenzoin sulfite, m.p. 126–128° (lit. m.p. 127–129°,[10] 131°[11]).

dl-**Hydrobenzoin Sulfite.**—To 5 g. of *dl*-hydrobenzoin and 4 g. of pyridine dissolved in 400 ml. of dry benzene, a solution of 2.9 g. of thionyl chloride in 20 ml. of benzene was added at room temperature in 1 hour. Stirring was continued for another hour, then the slurry was filtered (completely water-soluble residue, 5.5 g.; calcd. 5.4 g.). The benzene solution was washed with 1% sodium carbonate and dried over calcium chloride. The benzene was eliminated under reduced pressure, leaving 5.9 g. (97%) of residue, m.p. 80–84°. Crystallization from Skellysolve B (b.p. 60–70°) gave 5 g. of fluffy colorless needles, m.p. 84–86° (lit. m.p. 84°[11]).

cis-1,2-**Cyclohexanediol Sulfite.**—*cis*-1,2-Cyclohexanediol (10 g.) and 14 g. of pyridine were dissolved in 200 ml. of purified dioxane[12] and 10.4 g. of thionyl chloride in 100 ml. of dioxane was added in 90 minutes, keeping the temperature of the mixture at 15°. The pyridine hydrochloride was filtered off and the dioxane was eliminated from the filtrate by distillation at 20 mm. from a steam-bath, leaving 12.2 g. (88%) of residue, n^{20}_{D} 1.4852. It was purified by distillation to yield 10.6 g. of *cis*-1,2-cyclohexanediol sulfite, b.p. 90° (2 mm.), m.p. 6–8°, n^{20}_{D} 1.4832; d^{20}_{4} 1.2748; MR_D calcd. 37.14,[13] 37.01[14]; found 36.35 (lit. b.p. 126° at 20 mm.[15]).

Anal. Calcd. for $C_6H_{10}O_3S$: S, 19.77. Found: S, 19.47.

trans-1,2-**Cyclohexanediol Sulfite.**—By the same method as used for the preparation of the *cis*-sulfite, from 20 g. of *trans*-1,2-cyclohexanediol, 27 g. (97%) of crude sulfite was obtained, n^{20}_{D} 1.4860, which on distillation yielded 21 g. (76%) of product, b.p. 94–96° (2 mm.), m.p. −15°, n^{20}_{D} 1.4847, d^{20}_{4} 1.2654; MR_D calcd. 37.14[13], 37.01[14]; found 36.72 (lit. b.p. 122° at 20 mm.[15]).

Anal. Calcd. for $C_6H_{10}O_3S$: S, 19.77. Found: S, 19.42.

Pyrolysis of Cyclic Sulfites. **Pyrolysis of** *meso*-**Hydrobenzoin Sulfite.**—The decomposition of this sulfite was found to start at 200°, so 4.25 g. of the sulfite was heated at 240° for 10 minutes under nitrogen. The residue weighed 3.18 g. (calcd. for loss of sulfur dioxide, 3.20 g.) and gave a negative test for sulfur. It was treated with a saturated aqueous solution of sodium bisulfite, heating on a steam-bath for 10 minutes, then the mixture was diluted with water and extracted with ether. The aqueous layer, on acidification with dilute sulfuric acid, gave only a trace of oily material, showing that at most a trace of aldehyde was present in the pyrolysis mixture. The ether solution, on evaporation, left 3.09 g. of semi-solid substance. Treated with 10 ml. of 95% ethanol, it gave 1.2 g. of colorless crystals, m.p. 50–55°; recrystallization from ethanol raised the melting point to 57–59°.

The semicarbazone was prepared by heating under reflux an aqueous alcoholic solution of this product with semicarbazide hydrochloride and potassium acetate for one hour. Recrystallized from methanol, it melted at 145–148° (lit., desoxybenzoin, m.p. 60°; desoxybenzoin semicarbazone, m.p. 148°[16]).

The mother liquor of the product, m.p. 50–55°, gave, on treatment with semicarbazide hydrochloride and fractional crystallization, another 0.5 g. of desoxybenzoin semicarbazone, together with unidentified mixtures. The complete recovery of the desoxybenzoin from the pyrolysis products was not possible because of its low melting point and high solubility, but from this and other experiments it was assumed that 60 to 70% of the theoretical amount was formed.

Pyrolysis of *dl*-**Hydrobenzoin Sulfite.**—The decomposition temperature of this sulfite was found to be 215° and 2 g. of it was heated in a test-tube, bubbling nitrogen through it, for 15 minutes at 245°. The residue weighed 1.50 g. (theor. 1.51 g.) and was a light brown liquid, n^{20}_{D} 1.5934, which did not solidify even at −10°. One half of it was treated with saturated aqueous sodium bisulfite. It did not react in the cold, but on heating for a few minutes the organic layer disappeared and a mass of needles was formed.[17] Dilution with water gave a solution that was only slightly turbid.

The other half of the product was dissolved in 5 ml. of ethanol and 0.8 g. of semicarbazide hydrochloride and 1.2 g. of potassium acetate in 2 ml. of water were added. After heating on a steam-bath for 5 minutes, diluting with water and cooling, a crystalline precipitate was formed, which melted between 150 and 160°. One crystallization from benzene gave a product melting at 160–161°, so that it was evident that diphenylacetaldehyde (n^{21}_{D} 1.5920; semicarbazone m.p. 161–162°[18]) was the only important product formed in the pyrolysis, with a yield of at least 95%.

Stilbene Oxides.—*cis*- and *trans*-stilbene oxides were prepared by the method of Böeseken and Elsen,[19] based on the treatment of *cis*- and *trans*-stilbene in chloroform with the calculated amount of chloroform solution of perbenzoic acid at 0°: *cis*-stilbene oxide, m.p. 41–42°; *trans*-stilbene oxide, m.p. 66–68°. A sample of each was heated under exactly

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[6] As J. Read, I. G. M. Campbell and T. V. Barker, *J. Chem. Soc.* 2314 (1929), found, most of these prisms are individual crystals of the *dextro* and *levo* forms, which melt at 148°, while the racemic mixture melts at 120°.

[7] W. Markovnikov, *Ann.*, **302**, 22 (1898).

[8] M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 318 (1949).

[9] A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).

[10] Z. Kitasato and C. Sone, *Ber.*, **64**, 1142 (1931).

[11] D. Reulos and S. Le Tellier, *Compt. rend.*, **217**, 698 (1943).

[12] L. F. Fieser, "Experimental Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

[13] From bond refractions: A. I. Vogel, W. T. Cresswell, G. J. Jeffery and J. Leicester, *Chemistry & Industry*, 358 (1950).

[14] From atomic refractions: A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

[15] B. Tchoubar, *Bull. soc. chim.*, [5] **11**, 206 (1944).

[16] M. Tiffeneau, *Ann. chim.*, [8] **10**, 360 (1907).

[17] A. Breuer and T. Zincke, *Ann.*, **198**, 184 (1879), stated that diphenylacetaldehyde forms a sodium bisulfite adduct *only on heating*, as was found in this case.

[18] M. Tiffeneau, *Compt. rend.*, **142**, 1538 (1906).

[19] J. Böeseken and G. Elsen, *Rec. trav. chim.*, **47**, 694 (1938).

the same conditions as used for the pyrolysis of the hydrobenzoin sulfites. No change occurred and no depression in melting point was observed on mixing with samples of the pure oxides.

Pyrolysis of *cis*-1,2-Cyclohexanediol Sulfite.—Decomposition was found to start at 230°. A 10-ml. distilling flask was used, provided with a long neck, with the side-arm at a distance of 20 cm. from the bottom of the flask. The side-arm reached into a second 10-ml. distilling flask and the outgoing gases were passed through a 20% solution of sodium hydroxide to absorb sulfur dioxide. Nitrogen was bubbled through the liquid during the pyrolysis by means of a long capillary tube reaching to the bottom of the long-necked flask. The sulfite (2.30 g.) was heated at 265° for 45 minutes and at 300° for 15 minutes. No residue was left in the distilling flask and 1.36 g. (theor. 1.40 g.) of colorless distillate, n^{20}D 1.4528, had collected in the receiver. Analysis of the sodium hydroxide trap showed that it had absorbed 100% of the sulfur dioxide that the sulfite was able to liberate. Part of the distillate, on treatment with saturated sodium bisulfite solution, gave a crystalline solid which dissolved completely on dilution with water. The product distilled at 156–158°, except for a very small residue. The oxime was prepared by the standard method and melted at 89–90°. The product therefore was almost pure cyclohexanone (b.p. 156°, n^{20}D 1.4507; oxime m.p. 88°). Comparison of the infrared spectrum of the crude product of the pyrolysis with that of a sample of pure cyclohexanone also showed almost complete identity.

Pyrolysis of *trans*-1,2-Cyclohexanediol Sulfite.—Decomposition was found to start at 240°. The sulfite (5.7 g.) was pyrolyzed in the same long-necked flask used for the *cis* isomer. The temperature was raised from 250° to 300° in 70 minutes. At this time all the sulfur dioxide had been eliminated. Only some very dark resinous material remained in the flask and 3.1 g. of distillate had collected in the second flask (theor., after elimination of sulfur dioxide, 3.4 g.). The distillate was completely liquid at the end of the pyrolysis, but after a short time crystals started to form. After being left overnight, it had formed a solid mass of needles. This was heated with 5 ml. of methanol and, on cooling, 1.6 g. of colorless needles was obtained, m.p. 94–104°. Two recrystallizations from ethanol gave 1.35 g. of product, m.p. 126–128°.

Anal. Calcd. for $(C_6H_{10}O)_3$: C, 73.43; H, 10.26; mol. wt., 294. Found: C, 73.65; H, 10.51; mol. wt. 285 (cryoscopically in dioxane).

The crystalline material obtained accounted for 47% of the pyrolysis product, 52% of the distillate. Its infrared spectrum showed no carbonyl peak, but a strong ether peak at 9–9.2 μ.

The methanolic mother liquor on dilution with water and extraction with ether yielded, after elimination of the ether, a yellow oil. Extraction of this oil with sodium bisulfite gave, after acidification, only a trace of oily material. Attempts to cause the yellow oil to crystallize failed. When a vacuum distillation was tried, extensive decomposition with darkening occurred, and hardly any distillate came over.

Cyclopentaldehyde.—This aldehyde was prepared in rather low yield according to the method of Tiffeneau and Tchoubar.[20] Through a tube containing glass helices mixed with alumina and heated at 350°, 5 g. of *trans*-1,2-cyclohexanediol was distilled under 25 mm. pressure in a nitrogen stream. The distillate formed two layers. It was extracted with ether, washed with water and dried over magnesium sulfate. The residue left from the evaporation of the ether was fractionated under reduced pressure to produce 1.5 g. (34%) of cyclopentaldehyde, b.p. 77–80° (100 mm.), n^{20}D 1.4439.

When sulfur dioxide was bubbled through cyclopentaldehyde for 15 minutes, needles started to form. Left overnight the mixture crystallized completely, m.p. 85–90°. Two crystallizations from ethanol gave a product, m.p. 125–127°, giving no depression in melting point on mixing with solid obtained in the pyrolysis of *trans*-1,2-cyclohexanediol sulfite. Another sample of cyclopentaldehyde, on treatment with 30% nitric acid, solidified almost immediately, giving needles of m.p. 80–90°, rising to 126–128° on recrystallization. This material was identical to that from the pyrolysis of the *trans*-cyclohexanediol sulfite.

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[20] M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **199**, 1624 (1934).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Pyrolysis of Sulfites. III. Methyl Alkyl Sulfites. A New Method for the Preparation of Olefins

BY GIANCARLO BERTI[1]

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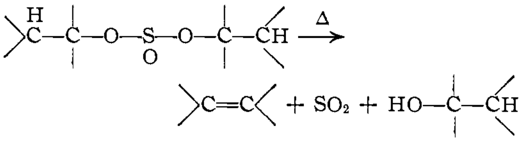
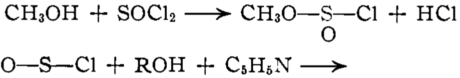
The pyrolysis of methyl alkyl sulfites has been investigated as a possible method for the preparation of olefins. Methyl α-methylphenethyl sulfite, methyl 3-phenylpropyl sulfite, methyl *cis*- and *trans*-2-phenylcyclohexyl sulfites, methyl *l*-menthyl sulfite and methyl cholesteryl sulfite were subjected to thermal decomposition and it was found that methyl *s*-alkyl sulfites give very good yields of olefins. The results are compared with those obtained in corresponding Chugaev reactions.

Introduction

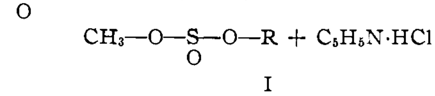
Previous work[2] had shown that olefins are formed as a principal product in the decomposition of organic sulfites. It was therefore considered promising to investigate the reaction specifically as a preparative method for olefins.


(1)

It would not be convenient to use symmetrically substituted sulfites for this purpose as in their pyrolysis only about half of the initial alcohol would be transformed into olefin, according to equation 1. The obvious solution to this was to use asymmetrically substituted sulfites, with one of the two substituents derived from an easily available alcohol. Methyl alkyl sulfites (I) were considered to be particularly appropriate for this purpose, due to the ease of preparation by reactions 2 and 3



$$CH_3OH + SOCl_2 \longrightarrow CH_3O\text{—}\underset{O}{S}\text{—}Cl + HCl \quad (2)$$



$$CH_3\text{—}O\text{—}\underset{O}{S}\text{—}Cl + ROH + C_5H_5N \longrightarrow CH_3\text{—}O\text{—}\underset{O}{S}\text{—}O\text{—}R + C_5H_5N{\cdot}HCl \quad (3)$$

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and to the fact that the methyl substituent could not give olefin in the pyrolysis, so that reaction 4 would be expected to take place predominantly.

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[1] E. I. du Pont de Nemours and Co. Fellow, 1952–1953. Abstracted from the Ph.D. dissertation of G. Berti, August, 1953. Present address: University of Pisa, Pisa, Italy.

[2] C. C. Price and G. Berti, THIS JOURNAL, **76**, 1207, 1211 (1954).