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, $n^{20}\mathrm{D}$ 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°, $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 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.

---

[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]

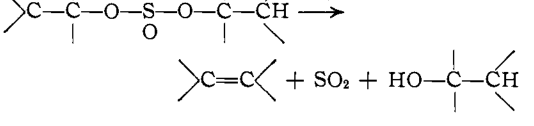
RECEIVED SEPTEMBER 17, 1953

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.

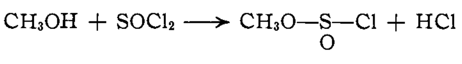
Introduction

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.

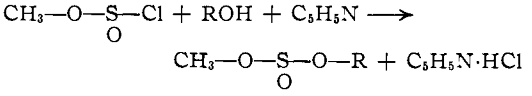
It would not be convenient to use symmetrically substituted sulfites for this purpose as in their pyrolysis only about half of the initial alcohol would be transformed into olefin, according to equation 1. The obvious solution to this was to use asymmetrically substituted sulfites, with one of the two 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



(1)



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



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

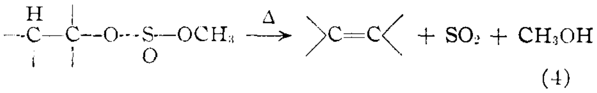
I

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.

---

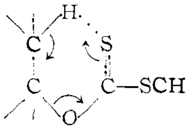
[1] E. I. du Pont de Nemours and Co. Fellow, 1952–1953. Abstracted from the Ph.D. dissertation of G. Berti, August, 1953. Present address: University of Pisa, Pisa, Italy.

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

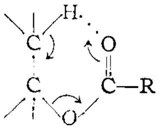


$$-\overset{H}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O-\underset{O}{S}-OCH_3 \xrightarrow{\Delta} \rangle C=C\langle + SO_2 + CH_3OH \quad (4)$$

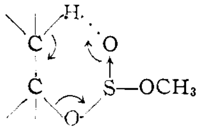
Another reason for the investigation of this type of elimination reaction was that a close similarity was expected between it and other pyrolytic elimination reactions, like that found in the Chugaev reaction and the thermal decomposition of esters. It is more or less generally accepted that these reactions take place by a concerted mechanism involving cyclic transition states, which in the case of Chugaev reaction will assume form II[3,4] and in the case of the pyrolysis of esters form III.[5]



II



III



IV

O'Connor and Nace[6] have shown recently that a number of other pyrolytic reactions, involving different xanthates, carbonates and carbamates, probably take place by the same mechanism. A similar cyclic transition state IV can be written also for the pyrolysis reaction of methyl alkyl sulfites.

The purpose of these preliminary experiments was therefore to investigate reaction 4 and to compare the results with those obtained in similar Chugaev reactions.

Experimental

Materials.—Commercial 3-phenylpropanol, *l*-menthol and cholesterol were used. α-Methylphenethyl alcohol was prepared by lithium aluminum hydride reduction of phenylacetone, as described before.[2]

cis-2-Phenylcyclohexanol was prepared by the method of Price and Karabinos,[7] involving hydrogenation of *o*-phenylphenol with Raney nickel in ethanol. A temperature of 100–105° and a pressure of 100–120 atm. were used to produce 74% of *cis*-alcohol, m.p. 30–40°, which was purified by crystallization from Skellysolve F at −10°, m.p. 40–42° (lit. m.p. 41–42°[7]).

trans-2-Phenylcyclohexanol was prepared by reduction of 2-phenylcyclohexanone with lithium aluminum hydride. *cis*-2-Phenylcyclohexanol was oxidized to 2-phenylcyclohexanone with chromic anhydride, following the method of Price and Karabinos.[7] The ketone (15.5 g.) in 60 ml. of dry ether was added dropwise to a stirred slurry of 1.4 g. of lithium aluminum hydride in 50 ml. of ether. The temperature was kept below 10° with an ice-bath. After the addition was completed, the mixture was stirred for another 15 minutes, then poured into ice-water, and enough 10% sulfuric acid was added to dissolve the precipitated aluminum hydroxide. The ether layer was washed with water and dried over sodium sulfate. The ether was evaporated and the oily residue poured, while still warm, into a funnel with a plugged outlet. After storage in the refrigerator, a mass of needles formed. The plug was removed and the oily impurities were eliminated by applying suction. The residual crystals were further purified by pressing them between filter paper to leave 9 g. of a product, m.p. 50–52° (lit. m.p. 56–57°[7]). By dissolving the oily fraction in very little petroleum ether and cooling at −10°, another 0.9 g. of product, m.p. 48–50°, was recovered (total yield 64%).

Methyl chlorosulfinate was prepared by the method of Carre and Libermann.[8] A 500-ml. three-necked round-bottomed flask, fitted with a mechanical stirrer, calcium chloride tube and dropping funnel was used. To 260 g. of thionyl chloride, 64 g. of anhydrous methanol was added dropwise with stirring during 45 minutes. The reaction mixture was left 48 hours at room temperature, to allow for the reaction to go to completion, then it was distilled under reduced pressure through a 50-cm. Vigreux column; the fraction boiling between 35 and 36° (65 mm.) was collected; yield 199 g. (88%). The product can be stored for some time in the refrigerator, but it slowly undergoes decomposition.[9]

General Procedure for the Preparation of Methyl Alkyl Sulfites.—Equimolar amounts of the alcohol and of methyl chlorosulfinate were used. A slight excess (1.1–1.2 moles) of pyridine was employed. Dry ether was commonly used as the solvent, but dioxane and benzene gave equally good results.

A solution of the alcohol and the pyridine was placed in a three-necked flask, provided with mercury-sealed stirrer and dropping funnel. Calcium chloride tubes surmounted the third neck and the top of the funnel. A solution of the chlorosulfinate was added slowly with stirring, controlling the temperature as stated in Table I. After the addition of the chlorosulfinate was completed, the stirring was continued for 30 minutes, then the precipitated pyridine hydrochloride was filtered off and the filtrate washed with 0.1 *N* HCl, with water and with 5% sodium bicarbonate. After drying over magnesium sulfate, the solvent was eliminated *in vacuo*. The residue may be purified by vacuum distillation or recrystallization. It also can be pyrolyzed without further purification.

Table I summarizes the results obtained.

TABLE I

PREPARATION OF METHYL ALKYL SULFITES

Compound	Reacn. temp., °C.	Yield,[a] %	B.p. or m.p., °C.	Mm.	$n^{20}D$	Sulfur, % Calcd.	Sulfur, % Found
V	0	75[b]	115–120	2	1.5068	15.0	14.8
VI	10	58 (89)[c]	132–134	2.5	1.5102	15.0	14.7
cis-VII	−5	80 (95)	148	1	1.5313	12.6	12.0
trans-VII	−5	75 (87)[d]	145 M. 48–50[e]	0.9	....	12.6	12.4
VIII	0	80 (90)	105–108	1	1.5640	13.7	13.7
IX	5	85	M. 115–117[f]		....	6.9	6.6

[a] Numbers in parentheses give yields of crude sulfite, the other yields of purified sulfites. [b] Some di-(α-methylphenethyl) sulfite, b.p. 175° at 0.5 mm., was formed in the distillation (lit. b.p. 168° at 0.3 mm.[2]). [c] About 25% of di-(3-phenylpropyl) sulfite, b.p. 221–223° (2.5 mm.), $n^{20}D$ 1.5428, was formed in the distillation (Carre and Libermann, *Compt. rend.*, 198, 274 (1934), give b.p. 248–254° at 11 mm.); some dimethyl sulfite also was formed in the same exchange reaction. [d] Some solid was left in the distillation, which, after crystallization from methanol, melted at 130–131°, probably di-(*trans*-2-phenylcyclohexyl) sulfite. [e] After crystallization from petroleum ether. [f] After crystallization from ethanol.

Pyrolysis Apparatus.—Two different methods were used for the pyrolysis of the sulfites. (A).—A simple distillation flask was used, with a capillary inlet for nitrogen, reaching to the bottom, and the side-arm connected to a receiver cooled in ice-water. Nitrogen was bubbled through the liquid during the pyrolysis. The outgoing gases were passed through a sodium hydroxide solution. This permitted following the course of the decomposition by withdrawing samples of the solution, neutralizing to phenolphthalein with acetic acid and titrating with standard iodine. When the decomposition temperature of the sulfite was not very much lower than its boiling point, it was found advisable to use a special distilling flask with a long neck (20-

---

[3] D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

[4] G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952).

[5] E. R. Alexander and A. Mudrak, *ibid.*, (a) **72**, 1810 (1950); (b) **72**, 3194 (1950); (c) **73**, 59 (1951).

[6] G. L. O'Connor and H. R. Nace, *ibid.*, **75**, 2119 (1953).

[7] C. C. Price and J. V. Karabinos, *ibid.*, **62**, 1159 (1940).

[8] P. Carre and D. Libermann, *Bull. soc. chim.*, [5] **53**, 1050 (1933).

[9] An attempt to speed up the reaction by adding pyridine hydrochloride, since the chloride ions are supposed to catalyze the second step of the reaction (P. D. Bartlett and H. F. Herbrandson, THIS JOURNAL, **74**, 5971 (1952)), was unsuccessful. After adding 0.5 g. of pyridine hydrochloride to the reaction mixture and leaving it overnight, the reaction flask was found almost empty, due to the formation of methyl chloride and sulfur dioxide. This is in accordance with the findings of Carre, *Bull. soc. chim.*, [4] **53**, 1075 (1933), who stated that the decomposition temperature of methyl chlorosulfinate in the presence of pyridine is −5°.

cm. or more distance from the side-arm to the bottom) to give some fractionation and avoid contamination of the distillate by sulfite.

(B).—A 50-cm. column of 1.5-cm. inside diameter, packed with glass wool and heated by means of a nichrome coil was used. At the top were a dropping funnel and an inlet for nitrogen. The sulfite was placed in the funnel and, after sweeping the column with nitrogen, it was dropped slowly into the column, in a slow stream of nitrogen. The bottom of the column was fitted to a distillation flask, the side-arm of which led into a receiver cooled in Dry Ice-acetone.

Analysis of Reaction Mixtures. (a) Total Olefin.—The total amount of olefin was determined by titration of a chloroform solution of the mixture with an acetic acid solution of bromine, according to the method of Uhrig and Levin.[10] It was estimated that this method gave an accuracy better than ±5% even with samples containing much non-olefinic material. When a sample of dimethyl sulfite was tested in the same conditions, it did not absorb bromine at a rate comparable to that of the olefins, although some decoloration took place after several hours. It was therefore assumed that the presence of some sulfite in the reaction products would not seriously interfere with the bromine titrations.

(b) **Mixtures of Propenylbenzene and Allylbenzene.**—A good qualitative test to detect propenylbenzene in allylbenzene was found to be the following: A slight excess of bromine is added to a chloroform solution of the olefin, the chloroform and the excess bromine are eliminated *in vacuo* and the residue is dissolved in acetone and treated with aqueous silver nitrate. The bromination product of propenylbenzene (1,2-dibromo-1-phenylpropane, a solid, m.p. 65°[11]) gives immediate precipitation, while that of allylbenzene (a liquid) gives only a slight turbidity and a definite precipitate only on standing for hours or on heating to the boiling point. Attempts to use this method for quantitative purposes, by employing standard solution of silver nitrate, gave rather inconsistent results.

It was therefore necessary to resort to the refractive index as a criterion for the analysis of mixtures of allylbenzene and propenylbenzene. The difference in refractive indices between these hydrocarbons is high enough to permit a rather accurate estimation of the composition of mixtures. There are some discrepancies in the literature as to the refractive indices of these olefins, but not very relevant ones. For propenylbenzene $n^{20}\text{D}$ 1.5492 was taken,[12] for allylbenzene, $n^{20}\text{D}$ 1.5110.[13]

As it could not be predicted *a priori* that in this case refractive indices would follow a linear relationship, it was found necessary to find out what deviations, if any, occur. By preparing a series of mixtures of allylbenzene and propenylbenzene in different proportions and plotting percentage of propenylbenzene against refractive index, it was found that all points were almost exactly on a straight line, so that the percentage of propenylbenzene in an unknown mixture containing only these two hydrocarbons is given by

$$\frac{n^{20}\text{D}(\text{obsd.}) - 1.5110}{1.5492 - 1.5110} \times 100$$

where $n^{20}\text{D}$ (obsd.) is the refractive index of the mixture. In samples that were slightly contaminated with dimethyl sulfite a correction of plus one unit in the third decimal place in $n^{20}\text{D}$ was applied for each 1% of dimethyl sulfite present.

(c) **Mixtures of 1-Phenylcyclohexene and 3-Phenylcyclohexene.**—A similar refractometric method was used for the determination of mixtures of these olefins. For 1-phenylcyclohexene $n^{20}\text{D}$ 1.5670 was used, according to Price and Karabinos[7] and to Alexander and Mudrak.[5a] There is some controversy on the refractive index of 3-phenylcyclohexene; a value of 1.5460 was used here, resulting from our repetition of the work of Alexander and Mudrak[5a] on the Chugaev reaction with *cis*-2-phenylcyclohexanol (see below). Alexander and Mudrak used a value of 1.5448, while Berlande[14] gives $n^{26}\text{D}$ 1.5440, which would correspond to about $n^{20}\text{D}$ 1.5464. Again a linear relationship was assumed between refractive index and composition.

(d) **Mixtures of 2-Menthene and 3-Menthene.**—The method of Hueckel, Tappe and Legutke[15] was used, based on the selective racemization of 3-menthene with *p*-toluenesulfonic acid, while 2-menthene is not affected by this reagent.

(e) **Hydroxyl Determination.**—The method of Freed and Wynne[16] was employed and found satisfactory. The presence of sulfite was found not to affect appreciably the accuracy of the method.

Pyrolysis Experiments. Pyrolysis of Methyl α-Methylphenethyl Sulfite (V). Method (A).—The decomposition of this sulfite was found to start at 245°. The sulfite (8 g.) was heated at 285° for 75 minutes. At the end of this time 97% of the theoretical amount of sulfur dioxide had been absorbed in the sodium hydroxide solution. The distillate weighed 5 g., $n^{20}\text{D}$ 1.5290, and 0.5 g. of tarry residue remained in the pyrolysis flask. The distillate was redistilled, collecting the fraction, b.p. 93–111° (97 mm.); 4.15 g. (95%), $n^{20}\text{D}$ 1.5312.

Anal. Dimethyl sulfite, 2%; α-methylphenethyl alcohol, 1%; total olefin, 96% (53% propenylbenzene, 43% allylbenzene).

Method (B).—Through the column heated at 340–350°, 21 g. of methyl α-methylphenethyl sulfite was dropped in about one hour. After all the liquid had been passed through, the system was swept with nitrogen for 15 minutes, then the column was taken off, the receiver was stoppered and heated on a steam-bath under a pressure of 5 mm. to bring all volatile products into the Dry Ice trap. A residue of 4 g. of unchanged sulfite was left in the flask. The liquid that had collected in the Dry Ice trap was dissolved in ether and washed with water to eliminate sulfur dioxide and methanol. After elimination of the ether, 9 g. of a liquid, $n^{20}\text{D}$ 1.5326, remained (96% based on unrecovered sulfite). The refractive index did not change after distillation from sodium.

Anal. Dimethyl sulfite, 1%; total olefin, 93% (55% propenylbenzene, 38% allylbenzene).

Base-catalyzed Reactions.—When 5 g. of methyl α-methylphenethyl sulfite and four drops of quinoline were heated, decomposition started at 160°, and after 80 minutes at 240° about 1 g. of tarry material remained in the distillation flask but only 70% of the calculated amount of sulfur dioxide had evolved. The yellow distillate (2.2 g.), after elimination of the methanol, had $n^{20}\text{D}$ 1.5215.

Anal. Dimethyl sulfite, 10%; α-methylphenethyl alcohol, 25%; total olefin, 60%.

A similar experiment in which pyridine hydrochloride was used as a catalyst instead of quinoline in the pyrolysis of 5 g. of the same sulfite, gave 3.0 g. of product, $n^{20}\text{D}$ 1.5110.

Anal. α-Methylphenethyl alcohol, 30%; total olefin, 40%.

Pyrolysis of Methyl 3-Phenylpropyl Sulfite (VI). Method (A).—A 6-g. sample of this sulfite was heated at 310–320° for 3 hours (decomposition started at 260°). The sulfur dioxide evolved corresponded to 85% decomposition.[17] Some black polymeric material was left in the flask, while the distillate, after washing with water, weighed 2.8 g., $n^{20}\text{D}$ 1.5042. Analysis for methyl sulfite showed that 10% of it was present. The product was distilled at 95 mm. and the hydrocarbon fraction, b.p. 93–105°, was collected, 1.9 g., $n^{20}\text{D}$ 1.5050.

Anal. Olefin, 80%; sulfite, trace.[18]

The olefinic product gave a negative test with bromine and silver nitrate, showing that at most only a trace of propenylbenzene was present.

The hydrocarbon fraction obtained in a similar experi-

---

[10] K. Uhrig and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

[11] L. Ruegheimer, *Ann.*, **172**, 131 (1874).

[12] A. Klages, *Ber.*, **36**, 2574 (1903).

[13] M. G. Voronkov, A. S. Broun and G. B. Karpenko, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 1927 (1949); *C. A.*, **44**, 1956 (1950).

[14] A. Berlande, *Compt. rend.*, **213**, 437 (1941).

[15] W. Hueckel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[16] M. Freed and A. M. Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).

[17] In a similar experiment the outgoing gases were passed through a solution of methone in 60% ethanol, heated at 60°. No precipitation occurred even on cooling, and on diluting with water only unchanged methone was recovered, which showed that no formaldehyde is formed in the pyrolysis.

[18] Most of the remaining 20% probably was *n*-propylbenzene.

ment was fractionated at ordinary pressure, taking fractions of approximately equal size.

Fraction	B.p., °C.	$n^{20}\mathrm{D}$
I	150–157	1.5020
II	157–158	1.5036
III	158–159	1.5042
IV	159–162	1.5064

This distillation gave evidence for the presence of a compound with a similar boiling point and a lower refractive index than that of allylbenzene (b.p. 156–157°, $n^{20}\mathrm{D}$ 1.5110), probably *n*-propylbenzene (b.p. 159°, $n^{20}\mathrm{D}$ 1.4925).

Method (B).—The pyrolysis tube was heated to 390°. Using 25 g. of methyl 3-phenylpropyl sulfite, 16 g. of it was recovered unchanged, while 6.6 g. of volatile products collected in the Dry Ice trap. After washing with water only 3.9 g. remained.

Anal. Olefin, 55%.

On distillation from sodium a product, b.p. 90–97° (95 mm.), $n^{20}\mathrm{D}$ 1.5096, was obtained. The refractive index would correspond to a mixture of 8% propylbenzene and 92% allylbenzene. Again the bromine–silver nitrate test for propenylbenzene was negative.

Pyrolysis of Methyl *cis*-2-Phenylcyclohexyl Sulfite (*cis*-VII). (a) **Crude Sulfite.**—The sulfite (14.5 g. of the crude undistilled product) was pyrolyzed by method A. Slight decomposition started at 170°. The temperature was raised from 170 to 255° in 70 minutes, then kept at 255° for 20 minutes, increasing the flow of nitrogen. The distillate weighed, after washing with water, 9.0 g., $n^{20}\mathrm{D}$ 1.5580. Redistillation gave 8.4 g. (93%) of liquid, b.p. 90° (2 mm.), 130° (16 mm.), $n^{20}\mathrm{D}$ 1.5607 (corresponding to 70% 1-phenylcyclohexene and 30% 3-phenylcyclohexene).

(b) **Purified Sulfite.**—The pyrolysis was repeated with 3.76 g. of redistilled methyl *cis*-2-phenylcyclohexyl sulfite, bubbling nitrogen through the liquid more rapidly than in the previous experiment. Decomposition started around 200° and distillation was complete in 40 minutes, raising the temperature from 235 to 270°. The distillate, after elimination of the methanol, had $n^{20}\mathrm{D}$ 1.5580 and, on redistillation from sodium, 2.3 g. of hydrocarbon (97%) was obtained, b.p. 240–250°, $n^{20}\mathrm{D}$ 1.5625, corresponding to 78% 1-phenylcyclohexene and 22% 3-phenylcyclohexene.

Anal. Olefin, 96%.

Pyrolysis of Methyl *trans*-2-Phenylcyclohexyl Sulfite (*trans*-VII).—The sulfite (3.4 g. of pure compound) was pyrolyzed by method A. Decomposition started at *ca.* 200°. Almost complete distillation took place after raising the temperature from 200 to 285° in 75 minutes (residue 0.06 g.). The distillate, after being washed with water, had $n^{20}\mathrm{D}$ 1.5560. It was redistilled at ordinary pressure, collecting the fraction boiling at 240–250°, 1.9 g. (89%), $n^{20}\mathrm{D}$ 1.5585. Redistillation from sodium raised the refractive index to 1.5598 (65% 1-phenylcyclohexene, 35% 3-phenylcyclohexene).

Anal. Olefin, 97%.

Chugaev Reaction with *cis*-2-Phenylcyclohexanol.—*cis*-2-Phenylcyclohexyl methyl xanthate, m.p. 45–46°, was prepared according to the method of Alexander and Mudrak[5a] and was pyrolyzed following exactly the instructions of the same authors. From 7.5 g. of the xanthate, 4.1 g. of crude product was obtained, which on distillation at 2.5 mm. gave the following fractions: (I) b.p. 86–90°, $n^{20}\mathrm{D}$ 1.5449; (II) b.p. 90–92°, $n^{20}\mathrm{D}$ 1.5452. The two fractions (3.9 g., 87%) were combined and distilled from sodium at atmospheric pressure, b.p. 235–236°, $n^{20}\mathrm{D}$ 1.5464.[19]

Isomerization of 3-Phenylcyclohexene during the Pyrolysis.—Pure *cis*-2-phenylcyclohexyl sulfite (1.70 g.) and 1.15 g. of 3-phenylcyclohexene ($n^{20}\mathrm{D}$ 1.5462, obtained in the Chugaev reaction) were heated under nitrogen for 30 minutes at 240°, then the temperature was raised to 270°, until all liquid had distilled. The distillate, 2.1 g. (calcd., 2.2 g.) after redistillation from sodium had $n^{20}\mathrm{D}$ 1.5568. The expected refractive index, if no isomerization of the 3-phenylcyclohexene had taken place and the pyrolysis of the sulfite had given the same mixture of olefins as described above, should have been $n^{20}\mathrm{D}$ 1.5532. Thus approximately 35% of the initial 3-phenylcyclohexene had isomerized to 1-phenylcyclohexene in the pyrolysis.

Pyrolysis of 1-Menthyl Methyl Sulfite (VIII). **Method** (A).—Pure *l*-menthyl methyl sulfite (5 g.) started to decompose at 215°. The temperature was raised from 215 to 275° in 1 hour before the distillation was complete. The colorless distillate, $n^{20}\mathrm{D}$ 1.4512, 2.8 g. (96%), gave negative test for sulfur, and distilled from sodium completely at 168–170°; $\alpha^{20}\mathrm{D}$[20] +73.05°, $[\alpha]^{20}\mathrm{D}$ +92°. Part of this product (2 g.) was heated under reflux on a steam-bath with 2 g. of absolute ethanol and 1 g. of *p*-toluenesulfonic acid for four hours. The solution was diluted with water, extracted with ether, the ether layer was washed with water and dried over calcium chloride. The ether was distilled and the residue distilled from sodium; $n^{20}\mathrm{D}$ 1.4514, $\alpha^{20}\mathrm{D}$ +28.8°.

The specific rotation of the mixture of menthenes obtained in the Chugaev reaction on *l*-menthol is reported as +114.77°[21] and +116.38°,[15] so that if it is assumed that the product of the Chugaev reaction is optically pure, the menthenes from the pyrolysis of the sulfite would be about 20% racemized. The method of Hueckel, Tappe and Legutke[15] for the analysis of mixtures of 2- and 3-menthenes can be applied only to the optically active fraction of the product. According to these authors the menthene obtained in the Chugaev reaction ($\alpha^{20}\mathrm{D}$ +91.0°), after the treatment with *p*-toluenesulfonic acid, had a rotation of $\alpha^{20}\mathrm{D}$ +28.1°, from which they deduced that 30% of 2-menthene was present. This was evidently based on the assumption that 2- and 3-menthene have the same optical rotation, but, as Hueckel himself reports,[15] 2-menthene has $\alpha^{20}\mathrm{D}$ +106°, and therefore 26% would have been a more accurate value. From this it is easily calculated that the optical rotation of 3-menthene should be +85° (assuming optical purity in the product of the Chugaev reaction). Using these values for the product of the sulfite pyrolysis, it is found that the concentration of optically active 2-menthene in it is 27%, that of optically active 3-menthene is 52%.

Method (B).—The temperature in the tube was kept at 340°, while 26 g. of crude, undistilled *l*-menthyl methyl sulfite was passed through it in 1 hour. The pyrolysis product was distilled under reduced pressure from a steam-bath into a Dry Ice trap. A residue of 2.8 g. of unchanged sulfite remained in the flask. The liquid in the Dry Ice trap, after being washed with water, weighed 10.8 g. (80%, based on unrecovered sulfite), $n^{20}\mathrm{D}$ 1.4510. Bromine titration showed that it contained 94% of menthenes. On redistillation from sodium it all boiled at 62–64° (18 mm.), $n^{20}\mathrm{D}$ 1.4513, $\alpha^{20}\mathrm{D}$ +52.8 g., $[\alpha]^{20}\mathrm{D}$ +66.0; after treatment with *p*-toluenesulfonic acid, $\alpha^{20}\mathrm{D}$ 22.6°. This indicated the following approximative composition: optically active 2-menthene, 21%; optically active 3-menthene, 35%; racemic menthenes, 44%.

Evidently the higher temperature used in method B had produced a more extensive racemization, involving the 3-menthene more than the 2-menthene. By considering the results of the two experiments together, it can be estimated that the over-all composition of the menthene mixture obtained in the pyrolysis of *l*-menthyl sulfite was about 65% of 3-menthene and 35% of 2-menthene.

Pyrolysis of Methyl Cholesteryl Sulfite (IX).—The sulfite (2.6 g.) was heated under a pressure of 20 mm. in a 10-ml. distilling flask, bubbling nitrogen through the liquid. Decomposition started at 185°. The temperature was raised from 185 to 270°, in 2 hours before all evolution of sulfur dioxide had stopped. The residue weighed 2.08 g. (theor., 2.08 g.) and was a yellow resin. It was extracted with 30 ml. of boiling absolute ethanol. On cooling, an oily material separated, which crystallized in the refrigerator. A second extraction with ethanol yielded another 0.4 g. of solid material, while some high-melting material remained undissolved (possibly dicholesteryl ether). The cholestadiene was purified by dissolving it in ether and precipitating

---

[19] These results check rather closely with those of Alexander and Mudrak,[5a] except that the yield of olefin was higher than that reported by them (71%) and the refractive index of the purified 3-phenylcyclohexene a little higher too. Berlande[14] reports b.p. 235°, $n^{26}\mathrm{D}$ 1.5440 for 3-phenylcyclohexene prepared by a completely different method.

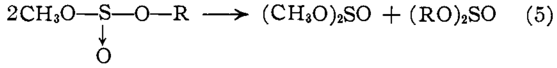
[20] In the following $\alpha^{20}\mathrm{D}$ will refer to the rotation of the pure liquid in a 10-cm. tube.

[21] L. Chugaev, *Ber.*, **32** 3335 (1899).

with ethanol; yield 1.1 g. (53%), m.p. 70-74°, α^{20}_D −81° (*c* 7.75, chloroform).[22]

Results and Discussion

The preparation of methyl alkyl sulfites did not present any difficulty and rather good yields of the crude sulfites were always obtained. The yields, however, decreased considerably when the sulfites were distilled, mainly because of the exchange reaction 5, taking place at higher temperatures.



$$2CH_3O{-}\underset{\downarrow\atop O}{S}{-}O{-}R \longrightarrow (CH_3O)_2SO + (RO)_2SO \quad (5)$$

Such an exchange reaction had been reported by Carre and Libermann.[8] This can, however, be obviated by direct pyrolysis of the crude sulfites, which are usually quite pure, and the yield and composition of the olefins is not appreciably affected by doing so. It is also necessary to take into consideration that reaction 5 may take place to a certain extent during the pyrolysis of the methyl alkyl sulfites, so that the products are liable to contain some dimethyl sulfite and also some of the alcohol formed by pyrolysis of the symmetrical sulfite, by reaction 1. This side reaction however was found not to be very important in secondary sulfites since, if the pyrolysis was conducted rapidly enough, only 1 to 2% of such side products were formed.

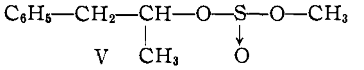
Table II summarizes the results obtained in the pyrolysis experiments. It can be seen that the yields of olefins from secondary alkyl methyl sulfites (V, *cis*- and *trans*-VII, VIII) were remarkably high. The yield of cholestadiene from IX would probably increase considerably if the chromatographic technique employed by O'Connor and Nace[4] were used for the separation.

TABLE II

PYROLYSIS OF METHYL ALKYL SULFITES

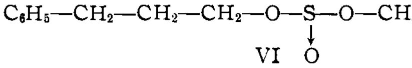
Compound	Dec. temp.,[a] °C.	Method	Yield of olefin, %	% Hofmann elimination[b] from Sulfite	Xanthate
V	245	A	92	45	
V		B	90	40	
V	160[c]	A	50		
VI	260	A	45[d]		
cis-VII	170[e]	A	93	30	
cis-VII	200[f]	A	93	22	96[g]
trans-VII	200	A	88	35	12[g]
VIII	215	A	95	35	30[h]
VIII		B	75		
IX	185		53[i]		

[a] Temperature at which decomposition begins. [b] Based on 100% olefin. [c] Catalyzed by quinoline. [d] All allylbenzene. [e] Crude sulfite. [f] Distilled. [g] Ref. 5a. [h] Ref. 15. [i] 3,5-Cholestadiene.



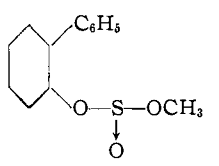
$$C_6H_5{-}CH_2{-}\underset{\displaystyle CH_3}{CH}{-}O{-}\underset{\downarrow\atop O}{S}{-}O{-}CH_3$$

V

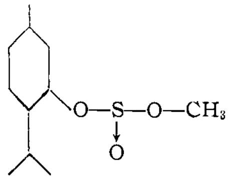


$$C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}O{-}\underset{\downarrow\atop O}{S}{-}O{-}CH_3$$

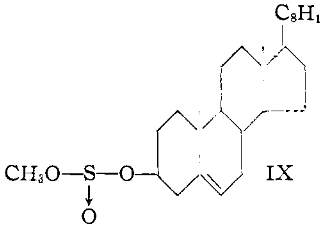
VI



VII

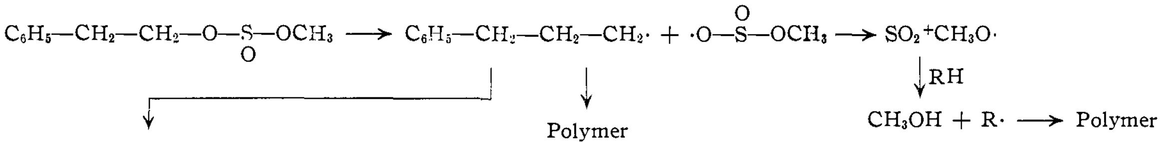


VIII



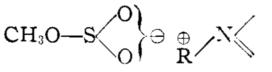
IX

The only case of primary alkyl methyl sulfite investigated (VI) gave a rather poor yield of olefin. This result was similar to those observed before[2] in the pyrolysis of symmetrical primary sulfites. Apparently in this case other reactions compete with reaction 4, as considerable amounts of methyl sulfite, polymeric material and probably some propylbenzene are found among the pyrolysis products. The higher percentage of methyl sulfite is a consequence of the higher temperature of pyrolysis for primary sulfites, which makes reaction 5 more important. Polymers and propylbenzene point strongly to a free-radical mechanism, such as

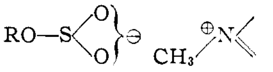


An alternative course for the methoxy radical would be disproportionation into formaldehyde and methanol, but no formaldehyde was found among the reaction products.

Organic bases, although they strongly depress the decomposition point of sulfite esters, did not give good results as catalysts. Thus only 50% of olefin was formed in the pyrolysis of V in the presence of quinoline. The pyrolysis product contained substantial amounts of dimethyl sulfite and α-methylphenethyl alcohol, pointing to a catalysis of reaction 5 by base, probably through the intermediate salts X and XI. Such salts could decompose by a Hofmann-type reaction 6 to give olefins and thus account for the lowering of the decomposition point of sulfites in the presence of bases. Intermediates of type X and XI were proposed by P. D. Bartlett to explain the base-catalyzed rearrangements of dimethyl and diethyl sulfite.[23]



X

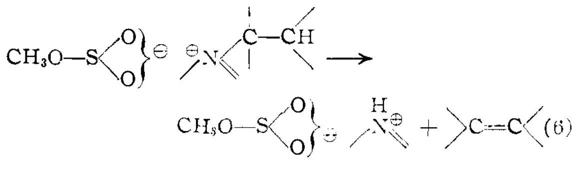


XI

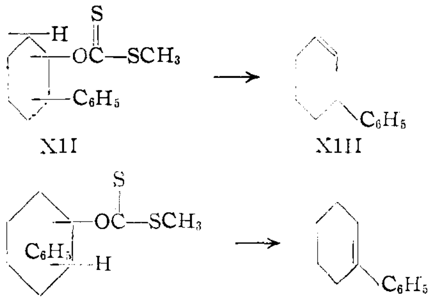
---

(22) Specific rotations ranging from −64 to −100°, m.p. from 70 to 79° are reported for 3,5-cholestadiene; see H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 567 (1937).

(23) W. E. Bissinger, F. E. Kung and C. W. Hamilton, THIS JOURNAL, **70**, 3940 (1948).


(6)

As far as the composition of olefin mixtures obtained in the pyrolysis of sulfites is concerned, in the case of V it was found that only 55 to 60% of the conjugated propenylbenzene was formed (Saytzeff-type elimination), while the rest was the unconjugated allylbenzene (Hofmann-type elimination). This indicated that the course of the reaction was unexpectedly independent of the conjugative influence of the phenyl group. On the other hand the results of the pyrolysis of *cis*- and *trans*-VII (which can be considered as cyclic equivalents of V) gave a different picture, since conjugation effects appeared to be much more important than steric effects, both isomers giving predominantly the conjugated 1-phenylcyclohexene. Still more surprising was the fact that the results obtained were completely different from those observed in the corresponding Chugaev reaction,[5a] as shown in Table II. The latter reaction proceeds substantially according to the theory of *cis*-elimination, the *cis*-xanthate (XII) giving predominantly the unconjugated 3-phenylcyclohexene (XIII), while the *trans*-xanthate (XIV) gives mostly the conjugated 1-phenylcyclohexene (XV). In the case of the sulfites, while *trans*-VII gave results about the same as those from the *trans*-xanthate, *cis*-VII was completely different, giving even less XIII than the *trans* isomer.


XII XIII

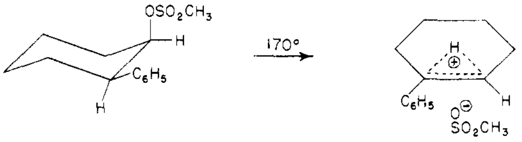
XIV XV

It therefore appears that the assumption of similar transition states in the pyrolysis of xanthates and of sulfites appears at least doubtful, although some other factors may account at least partly for the discrepancies.

The pyrolysis of sulfites has to be conducted at higher temperatures than that of the corresponding xanthates, so that thermal isomerization would be more likely to occur in the former case. Isomerization could also be brought about by traces of acidic impurities, more likely to be present in the sulfites than in the xanthates. Thus if the sulfites were slightly contaminated with the corresponding sulfates, these would give sulfur trioxide in the pyrolysis, which could act either as an elimination catalyst, or by isomerizing 3-phenylcyclohexene to 1-phenylcyclohexene. Some evidence for isomerization of the former to the latter olefin was found when a sample of pure 3-phenylcyclohexene was added to *cis*-VII before the pyrolysis. On the other hand, no evidence of isomerization of allylbenzene to propenylbenzene was found in the pyrolysis of VI.

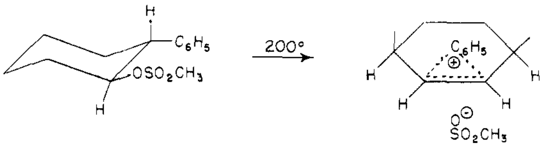
An alternative explanation for the differences in behavior of sulfites and xanthates would require the assumption of different mechanisms for the two types of pyrolyses. The dimensions of the methyl sulfite and of the methyl xanthate groups are probably quite different, and the fact that the latter fits well into a 6-membered cyclic transition state does not necessarily imply that the former fits into it as well.[24] The fact that those differences observed were in the opposite direction from the composition of olefins formed in the Chugaev reaction suggests that a mechanism quite different from the cyclic process proposed for the latter[5a] must be operative. In view of the evidence for ionic-type cleavage of the sulfite group in the glycol sulfites,[2] and since the composition of product obtained in the present investigation more nearly approximated that from phosphoric acid dehydration,[7] it seems likely that the mechanism here is ionic rather than cyclic.

For the *cis*-sulfite, the most likely conformation is equatorial phenyl and polar sulfite. As the carbon–oxygen bond ionizes, the polar *trans*-hydrogen can contribute an electron pair to form the bridged ion pair XVI, which can further decompose to 1-phenylcyclohexene by abstraction of either the bridged proton or the other proton indicated in formula XVI.[25]



cis-VII XVI

For the *trans*-sulfite, the most likely conformation is with both phenyl and sulfite equatorial, and the most likely structure for the ion pair one with a bridged phenonium ring,[26] XVII. Important factors to note in the case of the *trans* isomer are both the higher temperature required and the higher proportion of 3-phenylcyclohexene produced. These are convincing arguments against a cyclic process for the sulfite pyrolysis. The suggested bridged phenonium intermediate is proposed to account for the somewhat higher proportion of 3-phenylcyclohexene formed. In the ion XVII, it seems likely



trans-VII XVII

---

[24] Even in the case of the Chugaev reaction a different mechanism must sometimes be assumed, since Alexander and Mudrak[5c] found that olefins are formed even from xanthates with no *cis*-β-hydrogen.

[25] Mechanism proposed by C. C. Price. D. J. Cram (THIS JOURNAL, **74**, 2137 (1952)) has advanced arguments against the second alternative.

[26] The phenyl group is not in a favorable position to contribute to the transition and evidently does not since the *trans*-sulfite has a decomposition temperature 30° higher than the *cis* isomer.

that both the three-membered ring character and double bond character at ring carbons 1 and 2 might retard to some degree abstraction of a proton from these positions to give 1-phenylcyclohexene. There will, however, be hydrogens on atoms 3 and 6, with respect to the methyl sulfite anion and α to the partially unsaturated 1- and 2-positions, which might therefore be readily removable to produce 3-phenylcyclohexene. Cram[25] has presented some evidence that this mechanism is inoperative for E_1 reaction with 3-phenyl-2-butyl tosylates.

The mixture of methanes obtained in the pyrolysis of *l*-menthyl methyl sulfite (VIII) compared rather closely with that formed in the Chugaev reaction on *l*-menthol.

Conclusions

The experiments described suggest that the pyrolysis of methyl alkyl sulfites may be a useful procedure for dehydration, although the reaction has to be investigated further before its scope and limitations as a preparative reaction for olefins can be stated. Nevertheless, at this stage the following can be safely said.

(a) Yields are usually higher than in the Chugaev reaction. In the few cases so far studied several yields of better than 90% have been realized, while in the Chugaev reactions 70 to 80% is considered a good yield.

(b) The Chugaev reaction involves several steps (preparation of the sodium alcoholate, which in the case of secondary carbinols can be quite time-consuming, reaction with carbon disulfide and then with methyl iodide), and the xanthates are often difficult to purify. The preparation of methyl alkyl sulfites requires only one step, since methyl chlorosulfinate can be prepared separately and stored under refrigeration.

(c) The pyrolysis of xanthates is made very unpleasant by the evolution of carbon oxysulfide and methyl mercaptan. The product usually still contains substantial amounts of sulfurated impurities, and requires a lengthy purification. In the case of the sulfites, the only gas evolved is sulfur dioxide, which can be absorbed completely in alkali solutions; the olefinic product is quite pure and can be easily freed from the small amounts of dimethyl sulfite that may be present.

(d) The pyrolysis temperature of the sulfites, although higher than those of the corresponding xanthates, are much lower than those of the acetates. The latter require temperatures from 450 to 550°,[27] with consequent preparative difficulties and lower yields.

On the other hand, unfavorable features of the pyrolysis of sulfites are its apparent lack of stereospecificity and the fact that the yields drop sharply with primary substituents. The latter point, however, is a draw-back of all pyrolytic elimination reactions.

---

[27] J. P. Wibaut and A. J. van Pelt, *Rec. trav. chim.*, **57**, 1055 (1938); **60**, 55 (1941).

NOTRE DAME, INDIANA

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

The Polymerization of Stilbene in Boron Fluoride Etherate

BY CHARLES C. PRICE AND GIANCARLO BERTI[1]

RECEIVED SEPTEMBER 21, 1953

The previous report by Price and Meister[2] that *cis*-stilbene is isomerized to *trans*-stilbene by boron fluoride has been found to be in error. In the absence of a proton donor, no reaction occurs; in the presence of a proton donor, the reaction observed is the formation of a low-molecular weight polymer. When heavy water was employed as cocatalyst, the polymer contained about one deuterium atom, the recovered stilbene only a minor amount of deuterium.

Introduction

Price and Meister[2] in 1939, reported that boron fluoride would isomerize *cis*-stilbene to *trans*-stilbene. These findings have been questioned by Downing and Wright[3] and recently by Brackmann and Plesch,[4] who were unable to repeat this isomerization. The latter authors state that, if the reagents are dry and pure, no reaction at all takes place between *cis*-stilbene and boron fluoride. In the presence of a proton-donating co-catalyst, they report that *cis*-stilbene is transformed not into the *trans*-isomer, but into a low molecular weight polymer. We have therefore repeated our previous work, reinvestigating the behavior of *cis*- and *trans*-stilbene in boron fluoride etherate solution, a convenient homogeneous medium.

Experimental

cis-**Stilbene.**—This compound was prepared by decarboxylation of α-phenylcinnamic acid with copper chromite in quinoline, according to Taylor and Crawford.[5] For the purification the directions of Brackmann and Plesch[6] were followed, with some modifications. The crude product of the decarboxylation was distilled once at 0.005 mm., keeping the bath temperature at 90°. All of the distillate, except the first milliliter, was recrystallized twice from Skellysolve F, cooling in a Dry Ice–acetone-bath. In this way a 70–75% yield of a nearly colorless product, melting around 0°, n^{25}_{D} 1.6200, n^{20}_{D} 1.6218, was obtained, which was considered sufficiently pure for our purposes. Pure *cis*-stilbene, according to Brackmann and Plesch,[6] melts at 5–6° and has n^{20}_{D} 1.6214 ± 0.0005, but they report that after a few days the melting point drops to 0.6°. When the distillation was conducted at higher pressure a somewhat less pure product was obtained. Thus, using a pressure of 10 mm., a product was formed melting between −10 and −5°, n^{20}_{D} 1.6208. The slightly lower refractive index found for our product did not indicate the presence of *trans*-stilbene, as was shown by the following observation. A sample of *cis*-stilbene, n^{20}_{D} 1.6208, after saturation with *trans*-stilbene, had n^{20}_{D} 1.6230, showing that impurities of *trans*-isomer would in-

---

[1] E. I. du Pont de Nemours and Co. Fellow, 1952–1953. Abstracted from a part of the Ph.D. dissertation of G. Berti. Presented at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 7, 1953.

[2] C. C. Price and M. Meister, THIS JOURNAL, **61**, 1595 (1939).

[3] D. C. Downing and G. F Wright, *ibid.*, **68**, 141 (1946).

[4] D. S. Brackmann and P. H. Plesch, *J. Chem. Soc.*, 1289 (1953).

[5] T. W. J. Taylor and C. E. J. Crawford, *ibid.*, 1130 (1934).

[6] D. S. Brackmann and P. H. Plesch, *ibid.*, 2177 (1952).