

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## STUDIES OF CONJUGATED SYSTEMS. VI. THE PREPARATION OF THE GEOMETRIC ISOMERS OF METHYLSTYRYLCARBINOL AND OF PHENYLBUTADIENE

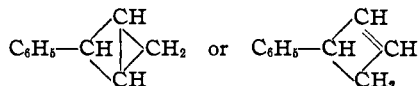
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In the course of an investigation on the addition reactions of conjugated systems we had occasion to study the preparation and properties of phenylbutadiene. In our early work with this hydrocarbon<sup>1</sup> we encountered considerable difficulty in obtaining consistent results. The yields of phenylbutadiene were at times very good, while again, with the same procedure and under apparently identical conditions, we failed to obtain any of the desired product. A search of the literature revealed that other investigators had encountered similar difficulties.<sup>2</sup> We therefore undertook a thorough study of the preparation of this hydrocarbon with the result that we were able to isolate the geometric isomers of both methylstyrylcarbinol and of phenylbutadiene and have determined the conditions under which to obtain either.

Phenylbutadiene was first prepared by Liebermann<sup>3</sup> by distilling allo-cinnamylidene-acetic acid under diminished pressure. He obtained a very low yield of this hydrocarbon, which distilled at 86° under 11 mm. pressure, and which absorbed two moles of bromine to give a tetrabromide. In a later paper he reported an improved method for the preparation of the same compound by heating cinnamylidene-malonic acid with quinoline.<sup>4</sup> A phenylbutadiene with the same properties was then prepared by Klages,<sup>5</sup> who treated cinnamic aldehyde with methylmagnesium iodide and dehydrated the methylstyrylcarbinol that was formed. Doebner<sup>6</sup> prepared a different phenylbutadiene by the dry distillation of cinnamyl-acrylic acid with barium hydroxide. This phenylbutadiene distilled at 120° under 10 mm. pressure and crystallized to a solid, m. p. 22°. It did not react with bromine, and this led Doebner to assign to it a cyclic structure to indicate its saturated nature.



<sup>1</sup> Muskat and Huggins, *THIS JOURNAL*, 51, 2496 (1929); Muskat and Grimsley, *ibid.*, 52, 1574 (1930); Muskat and Ludeman, *Ber.*, 62, 2284 (1929).

<sup>2</sup> Klages, *ibid.*, 39, 2591 (1906); Straus, *ibid.*, 42, 2882 (1909).

<sup>3</sup> Liebermann, *ibid.*, 33, 2400 (1900).

<sup>4</sup> Liebermann and Riiber, *ibid.*, 35, 2696 (1902).

<sup>5</sup> Klages, *ibid.*, 35, 2649 (1902); *ibid.*, 37, 2301 (1904).

<sup>6</sup> Doebner, *ibid.*, 35, 2129 (1902); *ibid.*, 36, 4318 (1903).

In 1904 Carl von der Heide<sup>7</sup> modified Klages' method for the preparation of phenylbutadiene, which modification has been used more or less satisfactorily ever since. His method is as follows: "To a solution of methylmagnesium bromide (prepared from 30 g. of magnesium) add drop by drop 100 g. of cinnamic aldehyde (instead of the theoretical 160 g.). After standing for twelve hours, decompose under strong cooling with 30% sulfuric acid, wash the ethereal solution with soda and water, dry and distil in a vacuum."

In our earlier work we used essentially the same procedure as that given by Carl von der Heide and obtained, as was stated above, inconsistent results. In order to ascertain the cause of our difficulties we have studied this reaction from every angle, varying every factor that might have some influence on the course of the reaction. The concentration of the Grignard reagent, the temperature at which the reaction occurred, and the rate of addition of the cinnamic aldehyde to the Grignard reagent were varied over a wide range without an appreciable effect on the products of the reaction. It was then discovered that the products obtained depended entirely on the decomposition of the intermediate Grignard addition compound and the treatment of the reaction product before distillation.

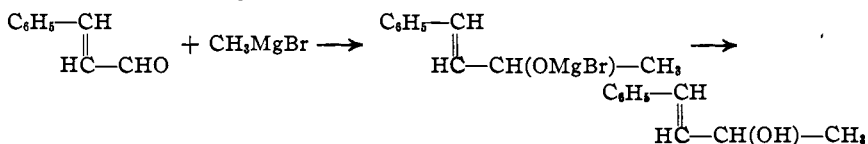
The intermediate Grignard addition compound was prepared according to the method described by Muskat and Ludeman<sup>1</sup> by treating cinnamic aldehyde with methylmagnesium bromide. If this intermediate Grignard addition compound, to which we shall refer as B, is decomposed with dilute acid and the acid is very carefully washed out of the ethereal solution before distillation, then a *new* methylstyrylcarbinol is formed which resists dehydration to a marked degree. The structure of this carbinol was proved by ozonization. This *new* methylstyrylcarbinol, although it has nearly the same boiling point as the methylstyrylcarbinol reported by Klages, is decidedly different. Klages' carbinol easily loses water, even on standing for a short time (frequently during distillation if a trace of acid is present), to give the ordinary phenylbutadiene, b. p. 86° under 11 mm. pressure.<sup>2</sup> The *new* carbinol has been kept for many months without the slightest decomposition. Only very strong dehydrating agents will dehydrate it to give, however, a *new* phenylbutadiene, b. p. 76° under 11 mm. pressure. That the two carbinols are true geometric isomers and not structural isomers was definitely established by the reduction of the two carbinols to give the same dihydro derivative, and by the results of an investigation of the chemical properties of the two carbinols, to be presented in a later paper.

If the intermediate B is decomposed with a large excess of 30% sulfuric acid and the acid is carefully washed out of the ethereal solution of the carbinol before distillation, then the new carbinol described above is

<sup>7</sup> Carl von der Heide, *Ber.*, **37**, 2101 (1904).

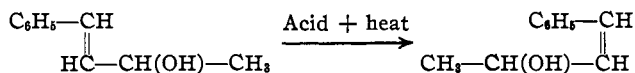
formed. However, if the acid is not washed out of the carbinol before distillation, a good yield of the ordinary phenylbutadiene is obtained.

It thus appears that the new carbinol is the normal reaction product of cinnamic aldehyde with methylmagnesium bromide. Inasmuch as cinnamic aldehyde is commonly supposed to have the *trans* configuration,<sup>8</sup> the new carbinol would be represented with the *trans* structure, since the preparation of the carbinol does not involve the double bond which is responsible for the geometric isomerism.



This *trans* structure of the new carbinol was further confirmed by comparing the rates of catalytic hydrogenation of the two carbinols.<sup>9</sup> (It was found that Klages' carbinol<sup>10</sup> was reduced at a faster rate than the new carbinol and according to Paal,<sup>11</sup> who showed that the *cis* isomer is always reduced more rapidly than the *trans* isomer, it would seem that the new carbinol has the *trans* configuration.) This has been confirmed in a similar manner by a study of the relative rates of oxidation of the two carbinols.

If the new *trans* carbinol is treated with dilute acids or even 30% sulfuric acid without heating, then it is neither rearranged to Klages' carbinol nor is it dehydrated to give phenylbutadiene. However, if some of the acid is allowed to remain dissolved in the carbinol, then on distillation it is partially rearranged to Klages' carbinol which, if 30% sulfuric acid has been used, loses water to give ordinary phenylbutadiene. We must then conclude that on warming with acids the *trans* carbinol is rearranged to the *cis* isomer.



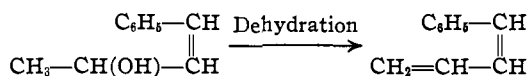
On standing, or in the presence of a dehydrating agent, the *cis* carbinol loses water readily to give Klages' phenylbutadiene, b. p. 86° under 11 mm. pressure. This phenylbutadiene must then have the corresponding *cis* structure.

<sup>8</sup> See M. Bourguel, *Bull. soc. chim.*, [4] 45, 1066 (1929), who has recently prepared the *cis* isomer of cinnamic aldehyde by the catalytic reduction of the corresponding acetylene derivative. It is planned to prepare a quantity of this new *cis*-cinnamic aldehyde, treat as above with methylmagnesium bromide and determine whether Klages' carbinol is the normal reaction product of this isomer.

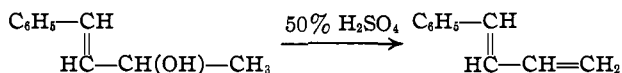
<sup>9</sup> This work will be reported in a paper that is to follow.

<sup>10</sup> Evidence to be given in the following paper leads us to believe that the carbinol reported by Klages was in reality a mixture of the two geometric isomers. However, we shall use the term "Klages' carbinol" to refer to that carbinol which easily loses water to form the ordinary phenylbutadiene.

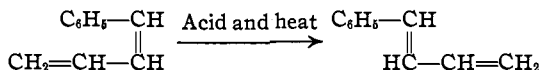
<sup>11</sup> Paal, *Ber.*, 60, 1221 (1927); *ibid.*, 63, 766 (1930).



If the *trans* carbinol is treated with a very strong dehydrating agent, such as 50% sulfuric acid, a molecule of water is lost to give a new phenylbutadiene, b. p. 76° under 11 mm. pressure. This must therefore have the corresponding *trans* structure.

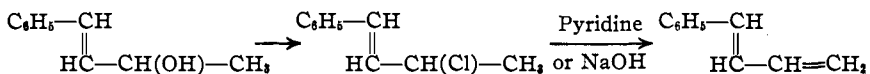


The *cis* and *trans* structures of the two phenylbutadienes as well as the carbinols have been confirmed by the relative rates of catalytic hydrogenation and of oxidation of the two isomers. In each case the isomer to which we have assigned the *cis* structure was hydrogenated more rapidly and oxidized more rapidly than was the *trans* isomer.<sup>9</sup> If the higher boiling *cis* phenylbutadiene is allowed to stand overnight with a trace of acid and then directly distilled, the lower boiling *trans* phenylbutadiene is formed. Obviously the acid rearranges the *cis* phenylbutadiene to the *trans* isomer, while it rearranges the *trans* methylstyrylcarbinol to the *cis* isomer.



If methylmagnesium iodide is used to react with cinnamic aldehyde instead of methylmagnesium bromide the conditions are somewhat different. These details are described in the experimental part.

The new *trans* phenylbutadiene can be prepared by treating the *trans* carbinol with dry hydrogen chloride in anhydrous ether solution to form an almost quantitative yield of the chloride. The chloride may now be refluxed for several hours with pyridine or shaken for twenty-four hours with a 5% sodium hydroxide solution at room temperature, either of which removes one mole of hydrogen chloride to give the new *trans* phenylbutadiene in an almost quantitative yield.



In the experimental part the method for the preparation of each of the methylstyrylcarbinols and of the phenylbutadienes will be given in detail.

It is interesting to note that the most striking chemical difference between the two methylstyrylcarbinols lies in the fact that they differ in the ease with which water is lost to give the corresponding phenylbutadiene; yet the geometric difference, the *cis-trans* isomerism, has apparently nothing to do with the tendency to lose water. It is at once clear why *cis* maleic acid should lose water easily to give an anhydride while the *trans* fumaric should not, but it is difficult to understand why there should be

any difference in the ease with which water is lost from the two methylstyrylcarbinols, since the part of the molecule affected supposedly has nothing to do with the geometric isomerism. It may be that the phenyl group in the *cis* position has a loosening influence on the hydrogen atoms of the methyl group. This suggestion finds some support in the fact that the hydroxyl group of the *trans* carbinol seems to be fully as reactive as the hydroxyl group of the *cis* carbinol, and therefore the difference in the ease of eliminating water from the two carbinols must depend on the hydrogen atoms of the methyl group.

### Experimental Part<sup>12</sup>

**The Preparation of the Intermediate Grignard Addition Compound B.**—The intermediate Grignard addition compound was prepared according to the method of Muskat and Ludeman.<sup>1</sup> "Methylmagnesium bromide is prepared in the usual manner from 40 g. of methyl bromide and 10 g. of magnesium. The manipulation is much easier and the loss is much less if the methyl bromide is allowed to pass into the ether suspension of the magnesium turnings as a gas from a cylinder instead of added as a liquid (b. p. 4.5°) through a dropping funnel. Thirty grams of cinnamic aldehyde (free of cinnamic acid and dried over calcium oxide) is allowed to drop in slowly, the reaction flask being immersed in an ice-salt mixture during the process. The theoretical amount of cinnamic aldehyde (53 g.) is not used, for only part of the cinnamic aldehyde combines with the Grignard reagent; the rest polymerizes to a resin. . . ." In this work we used three times the quantities of the reagents given above, and the addition compound was allowed to stand overnight before decomposition. The Grignard addition compound prepared in this way will be referred to as B.

### Decomposition of the Intermediate Grignard Addition Compound B

(a) **With Dilute Acids. The Preparation of *Trans* Methylstyrylcarbinol.**—The intermediate Grignard addition compound B was decomposed with sufficient dilute (about 10%) acid (sulfuric, hydrochloric or acetic acid may be used) to dissolve the magnesium hydroxide. The decomposition was effected by gradually pouring the intermediate B into a large flask containing a mixture of ice and dilute acid. A mechanical stirrer was used to keep the mixture in constant agitation and thus avoid localized heating. The decomposition mixture was extracted with ether, the ethereal solution very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a small fraction, distilled over completely at 117° under 4 mm. pressure. Its boiling point was determined at several pressures: 116.5° at 3.5 mm., 117.5° at 5 mm., 123° at 7.5 mm. pressure. It is a stable compound and may be kept for many months without the slightest decomposition. Its refractive index at 31° is 1.5550.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O: C, 81.03; H, 8.16. Found: C, 81.02, 81.03; H, 8.20, 8.21. Calcd. for C<sub>10</sub>H<sub>12</sub>O: mol. wt., 148.09. Found: mol. wt., 149.1.

The method of preparation and the above analyses indicate that the compound is methylstyrylcarbinol, C<sub>6</sub>H<sub>5</sub>—CH=CH—CH(OH)—CH<sub>3</sub>; however, its chemical and physical properties are at variance with those of the methylstyrylcarbinol reported

<sup>12</sup> The authors wish to express their appreciation to Mr. Charles Marshall for his aid in the preparation of some of these compounds.

by Klages.<sup>5</sup> That it really is a methylstyrylcarbinol was proved by subjecting it to ozonization. The carbinol (10 g.) was dissolved in chloroform and a current of ozonized oxygen was bubbled through the solution for several hours. An ozonizer similar to the one described by Harries<sup>13</sup> was used. After the ozonization was complete the chloroform was removed by vaporization under reduced pressure and the residual viscous ozonide was decomposed with water. To insure the complete decomposition of the ozonide it was warmed on the water-bath for a short time. The mixture consisted of aldehydes and acids and was separated into its components by extracting the alkaline solution several times with ether. The ethereal solution was dried and the ether removed by vaporization. A solid (0.9 g.) remained which melted at 120°. It was crystallized once from water and melted at 122°, the melting point of benzoic acid. A mixture with pure benzoic acid also melted at 122°. The water extract gave a positive Uffelman test for lactic acid, the second oxidation fragment of the carbinol.

The ethereal solution of the aldehydes was again washed with alkali and the ether was removed by vaporization. The residue, an oil, was treated with an aqueous solution of semicarbazide hydrochloride in the usual manner. A semicarbazone (8.8 g.) was precipitated after a time. This was removed and dried. It melted at 209°. It was recrystallized several times from alcohol and melted at 214°, the melting point of the semicarbazone of benzaldehyde. When it was mixed with the synthesized product the melting point of the mixture was not lowered. This corresponds to a 90.8% yield of benzaldehyde.

It is of paramount importance for the preparation of this *trans* methylstyrylcarbinol to wash all traces of acids from the ethereal solution of the carbinol before distillation. It is also better to use anhydrous sodium sulfate rather than calcium chloride to dry the ethereal solution, since frequently traces of acid may be introduced by the calcium chloride.

The above preparation was repeated except that the acid was not washed out of the ethereal solution of the carbinol before distillation. On distilling the residual oil a mixture of the *trans* carbinol and a small amount of Klages' *cis* carbinol was obtained. The presence of the latter was indicated by the fact that the distillate became cloudy shortly after distillation. The cloudiness is due to the water split from the *cis* carbinol. The ready loss of water is a characteristic property of this compound. Frequently during distillation a portion of the *cis* carbinol will decompose to give phenylbutadiene and droplets of water. We must therefore conclude that the *trans* carbinol rearranges to the *cis* carbinol when it is warmed in the presence of acid.

That this rearrangement is due to the warming with acid and not merely to the presence of acid was confirmed in the following manner. The pure *trans* carbinol was shaken with 30% sulfuric acid at room temperature (about 25°) for twelve hours. It was then divided into two portions. The first portion was extracted with ether, the ethereal solution was very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether was removed by vaporization. The residual oil distilled over completely at 117° under 4 mm. pressure without the slightest indication of the presence of any *cis* carbinol. The second portion was worked up in exactly the same way except that the acid was not all washed out of the carbinol before distillation. During the distillation of the residual oil a great deal of water was split out and a mixture of phenylbutadiene, *cis* carbinol, droplets of water and some *trans* carbinol distilled over. This proves conclusively that it is necessary to warm the *trans* carbinol with acid to cause a rearrangement to take place.

(b) With Water.—The intermediate B was hydrolyzed with water, the hydrolysis product was extracted with ether, the ethereal solution dried over anhydrous sodium

<sup>13</sup> Houben-Weyl, "Die Methoden der Organischen Chemie," 1924, Vol. III, p. 276.

sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a very small fraction, distilled at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described above.

The yield of the carbinol is much less and the manipulation more difficult by this method than by the method described above using dilute acids to decompose the intermediate B, since the magnesium hydroxide, which results from the hydrolysis of the intermediate B, frequently forms a stable emulsion with the ethereal solution of the carbinol.

(c) With 30% Sulfuric Acid. The Preparation of Ordinary *Cis* Phenylbutadiene.—The intermediate B was decomposed with 30% sulfuric acid exactly as described in (a). The decomposition mixture was extracted with ether, the ethereal solution very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure the residual oil, with the exception of a small fraction, distilled over at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described in (a).

The above preparation was repeated except that the acid was not washed out of the ethereal solution of the carbinol before distillation. On distilling the residual oil a mixture of the ordinary phenylbutadiene, the *trans* and *cis* carbinols and droplets of water was obtained. A considerable portion of the oil distilled at 204° under 3 mm. pressure, which is the boiling point of the dimer of phenylbutadiene. It was observed that whenever the *cis* phenylbutadiene was formed in the course of such a reaction, polymerization occurred to a marked degree.

In order to obtain a good yield of phenylbutadiene the following procedure was used. The intermediate B was poured into a beaker containing a liter of 30% sulfuric acid and no effort was made to keep the reaction cold. It was allowed to stand in contact with the acid overnight. The decomposition product was then extracted with ether, the ethereal solution washed several times with water and dried over anhydrous sodium sulfate overnight. The ether was then removed by vaporization and the residual oil subjected to distillation under reduced pressure. A 60% yield of phenylbutadiene boiling at 86° under 11 mm. pressure, was obtained. It was identical with the phenylbutadiene reported by Klages. Its refractive index at 28° is 1.5950.

It may be well to emphasize the following points in this method for the preparation of *cis* phenylbutadiene. If the intermediate B is decomposed with 30% sulfuric acid under strong cooling and continuous stirring and all of the acid is washed out of the ethereal solution before distillation, then the *trans* methylstyrylcarbinol is formed. If the intermediate B is decomposed with 30% sulfuric acid and no effort is made to cool the reaction or to keep it agitated to prevent localized heating, then the heat of the reaction in the presence of the acid is sufficient to rearrange the *trans* to the *cis* carbinol. Once rearrangement has taken place then the length of contact with the drying agent becomes of paramount importance. If the acid is washed out of the ethereal solution, and the solution is dried but a short time, the *cis* carbinol is the main product of the reaction. If, however, the acid is not washed out, then some decomposition occurs and phenylbutadiene, *cis* carbinol and water result. If the acid is washed out of the ethereal solution after the above rearrangement and the solution is dried overnight, then *cis* phenylbutadiene is obtained. If the acid is not washed out of the ethereal solution and the solution is dried overnight, then on distillation the *cis* phenylbutadiene may be rearranged into the *trans* phenylbutadiene, as will be shown later in the paper.

(d) With 50% Sulfuric Acid. The Preparation of *Trans* Phenylbutadiene.—The intermediate B was decomposed with 50% sulfuric acid in a manner entirely analogous to that described in (a). The residual oil was distilled under diminished pres-

sure. A small amount of oil distilled at 76° under 11 mm. pressure and a dark viscous mass remained in the distilling flask. The oil was analyzed and proved to be a lower-boiling phenylbutadiene. Its refractive index at 28° is 1.5920.

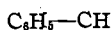
*Anal.* Calcd. for  $C_{10}H_{10}$ : C, 92.25; H, 7.75. Found: C, 92.11, 92.21; H, 8.09, 7.90. Calcd. for  $C_{10}H_{10}$ : mol. wt., 130.08. Found: mol. wt., 132.2.

That it is the *trans* isomer of phenylbutadiene was shown by a study of its chemical reactions, which will be presented in a later paper.

The new *trans* phenylbutadiene can be prepared in a good yield by either of the two following methods.

(1) The *trans* carbinol was dissolved in anhydrous ether and dry hydrogen chloride gas was passed in until no more was absorbed. The flask was immersed in an ice-bath during the reaction. The ethereal solution was washed with dilute alkali to remove the excess acid and then with water until neutral. It was dried over anhydrous sodium sulfate and the ether was removed by vaporization. Upon distillation of the residual oil under diminished pressure, an almost quantitative yield of a light yellow oil distilled at 104° under 6 mm. pressure. It is quite stable and may be kept for several weeks with but little decomposition.

*Anal.* Calcd. for  $C_{10}H_{11}Cl$ : Cl, 21.29. Found: Cl, 21.17, 21.21.



The chloride has the structure  $HC(=CH_2)-CHCl-CH_3$ . A thorough study of the chemical reactions of this chloride has been made and these will be presented in a later paper.

The chloride was refluxed for several hours with five volumes of pyridine. The reaction mixture was taken up in ether and washed thoroughly with water to remove the pyridine. The ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by vaporization. When subjected to distillation under diminished pressure, the residual oil distilled over almost completely at 76° under 11 mm. pressure, the boiling point of the *trans* phenylbutadiene.

The chloride may be converted into the *trans* phenylbutadiene by shaking for twenty-four hours with approximately twice the theoretical amount of 5% sodium hydroxide. The reaction mixture is extracted with ether, the ether solution washed until neutral, dried over anhydrous sodium sulfate and the ether removed by vaporization. Upon distillation of the residual oil an almost quantitative yield of *trans* phenylbutadiene is obtained.

(2) The *trans* phenylbutadiene may be prepared by rearranging the *cis* phenylbutadiene. The rearrangement may be effected by allowing the *cis* phenylbutadiene to stand overnight with a trace of acid. A few pieces of calcium chloride moistened with dilute hydrochloric acid are added to the *cis* phenylbutadiene and, after standing overnight, the compound is distilled under reduced pressure. The lower-boiling *trans* phenylbutadiene distills at 76° under 11 mm. pressure. The yield is quantitative.

**The Preparation of the Intermediate Grignard Addition Compound I.**—The intermediate Grignard addition compound I is prepared in exactly the same manner as the intermediate Grignard addition compound B, except that methylmagnesium iodide is used in place of methylmagnesium bromide. The intermediate I is much less soluble in ether than is the intermediate B.

**Decomposition of the Intermediate Grignard Addition Compound I.**—The intermediate I was decomposed with dilute sulfuric acid in a manner entirely analogous to that described above for the corresponding methylmagnesium bromide intermediate B. The decomposition mixture was extracted with ether and the ethereal solution was washed with sulfurous acid to reduce the iodine that was set free. The intermediate



It may be decomposed directly with a saturated solution of sulfurous acid and thus avoid the preliminary treatment with dilute acid. After all of the iodine had been removed the ethereal solution was washed with water until neutral. A large number of washings were required to remove all of the sulfurous acid. The ethereal solution was dried over sodium sulfate and the ether removed by vaporization. When subjected to distillation under reduced pressure, the residual oil distilled over almost completely at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described above.

**The Preparation of *Cis* Methylstyrylcarbinol.**—The above preparation was repeated except that the ethereal solution of the carbinol was washed only twice with water before distillation, thus leaving some of the sulfurous acid in solution. On distilling the residual oil, the *cis* methylstyrylcarbinol was obtained, b. p. 144° under 21 mm. pressure. It was identified by its characteristic tendency to lose water.

*Anal.* Calcd. for  $C_{10}H_{12}O$ : C, 81.03; H, 8.16. Found: C, 81.12, 81.10; H, 8.30, 8.27. Calcd. for  $C_{11}H_{12}O$ : mol. wt., 148.09. Found: mol. wt., 150.0.

This method is the most reliable for the preparation of *cis* methylstyrylcarbinol. Its refractive index at 31° is 1.5536.

If the above method of preparation is repeated and none of the acid is washed out, then on distilling the residual oil a small yield of the *trans* phenylbutadiene is obtained, and a dark viscous polymer remains in the distilling flask.

### Summary

1. The isolation of the geometric isomers of methylstyrylcarbinol have been given and their geometric structures determined.
2. The isolation of a new geometric isomer of phenylbutadiene is given.
3. The geometric structures of the two isomeric phenylbutadienes were determined.
4. Methods for the preparation of each of the geometric isomers of methylstyrylcarbinol and of phenylbutadiene are described.
5. Methods of rearranging the above geometric isomers are given.

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## STUDIES OF CONJUGATED SYSTEMS. VII. THE CHEMICAL REACTIONS OF THE GEOMETRIC ISOMERS OF METHYLSTYRYLCARBINOL

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In the preceding article<sup>1</sup> we gave a detailed description of the methods of preparation of the geometric isomers of methylstyrylcarbinol and of the corresponding phenylbutadienes. The present paper contains the results of an investigation of the chemical reactions of the two geometric isomers of methylstyrylcarbinol.

The reactions studied have been of two general types: *i. e.*, reactions of the hydroxyl group, and reactions involving the double bond. In the

<sup>1</sup> Muskat and Herrman, *THIS JOURNAL*, 53, 252 (1931).