

I 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 $C_{11}H_{12}O$: 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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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

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

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In the preceding article¹ 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

¹ Muskat and Herrman, *THIS JOURNAL*, 53, 252 (1931).

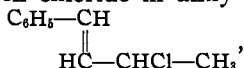
following pages we shall present, under these two heads, a comparison of the behavior of the two geometric isomers of methylstyrylcarbinol.

I. Reactions of the Hydroxyl Group

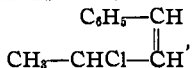
Klages² reported the preparation of the phenylurethan, m. p. 94°, of his *cis* carbinol. We have been unable to duplicate his results with the pure *cis* carbinol, although the *trans* carbinol does give a quantitative yield of a phenylurethan of the same melting point and apparently of the same crystalline structure. Therefore it seems evident to us that the results reported by Klages were obtained on a mixture of the two carbinols rather than from the pure compound. It must be remembered that Klages was not aware of the existence of the *trans* isomer of methylstyrylcarbinol.

Burton³ also reported a phenylurethan, m. p. 94°, from methylstyrylcarbinol prepared by Klages' method. In addition Burton reported the preparation from his carbinol of an acetate which is identical with the acetate we prepared from the *trans* carbinol. The *cis* carbinol is dehydrated under the conditions used to prepare the acetate of the *trans* carbinol. This is confirmatory evidence for our previous statement that the urethan reported by Klages resulted from the *trans* carbinol. It is significant that the previous investigators of methylstyrylcarbinol, who were unaware of the existence of geometric isomers of methylstyrylcarbinol, frequently purified their product in such a manner as to remove any *cis* carbinol present in the mixture they first obtained.

The *trans* carbinol, when treated with dry hydrogen chloride in anhydrous ether solution, reacts to form a *trans* chloride,



b. p. 104° under 6 mm. pressure. Under the same conditions the *cis* carbinol reacts with hydrogen chloride to form a *cis* chloride,



b. p. 108° under 6 mm. pressure. Klages² has reported the preparation in a similar manner of a chloride from his methylstyrylcarbinol, but he stated that the chloride was so unstable that he was able neither to distil it nor to obtain even an approximate analysis. We have found that if all of the excess hydrogen chloride is not washed out of the ethereal solution of the chloride before distillation, then the chloride decomposes during distillation. However, if the acid is carefully washed out, then the chlorides of either of the carbinols may be distilled without the slightest decomposition. It is interesting to note that hydrogen chloride did not add to the double bond of either of the carbinols. The chloride obtained from the *cis* carbinol was found to be identical with the chloride obtained from the addition of hydrogen chloride to the *cis* phenylbutadiene.⁴

² Klages, *Ber.*, 35, 2649 (1902).

³ Burton, *J. Chem. Soc.*, 132, 455 (1929).

⁴ To be reported in a later paper.

The *trans* chloride was refluxed with a 10% solution of sodium acetate for several hours. A product was obtained which distilled at 118° under 4 mm. pressure, and which was identified as the acetate, C_6H_5-CH

$\begin{array}{c} || \\ HC-CH(OC_2H_5O)-CH_3 \end{array}$. This acetate is identical with the acetate prepared directly from the *trans* carbinol as given above. A condensation product of the *trans* carbinol was also obtained. This condensation product will be referred to later in the paper.

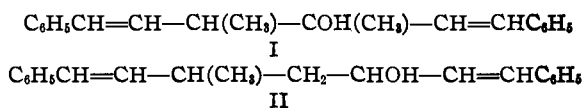
When the *trans* chloride was refluxed with silver oxide until all of the chloride had reacted, a small amount of the *trans* phenylbutadiene, b. p. 76° under 11 mm. pressure, was obtained with a preponderance of the polymer of this phenylbutadiene, b. p. 194° under 3 mm. pressure.

The *trans* chloride was refluxed with about five times its volume of pyridine for several hours. An almost quantitative yield of the *trans* phenylbutadiene, b. p. 76° under 11 mm. pressure, was obtained. Under the same conditions the *cis* chloride gave about 40% of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure, the rest being polymerized to the dimer.

The *trans* chloride was shaken with two moles of 5% sodium hydroxide for approximately twenty-four hours. An almost quantitative yield of the *trans* phenylbutadiene was obtained. Under the same conditions the *cis* chloride gave a very small amount of the *cis* phenylbutadiene, the rest being polymerized to the dimer.

The reactions of the carbinols with varied concentrations of sulfuric acid to cause rearrangement or dehydration have been amply discussed in the preceding paper.¹

In addition to these reactions of the hydroxyl group of the carbinols it has been observed that on heating the *trans* carbinol, condensation occurs with the elimination of one mole of water from two moles of the carbinol. The condensation product distils over at 200° under 6 mm. pressure. It may have either of the following structures (the geometric isomerism will not be indicated).



On ozonization it was possible to isolate 76.3% of benzaldehyde calculated on the basis of two moles of benzaldehyde for each mole of the condensation product. This proves that the condensation did not involve the double bonds. The condensation product also formed a tetrabromide, m. p. 179°, which confirms the above conclusion. Structure I is favored due to the fact that the hydrogen atoms of the terminal methyl group of the *trans* carbinol are very unreactive. No effort was made to distinguish between

the two structures. Under the same conditions the *cis* carbinol decomposed to give water and the dimer of phenylbutadiene.

II. Reactions Involving the Double Bond

An effort was made to prepare the dibromide addition compounds of the two carbinols. The conditions of bromination were widely varied but in every case decomposition occurred with the elimination of water and the formation of the tetrabromide of phenylbutadiene.

The catalytic hydrogenation of the two carbinols by means of the Adams method⁵ was studied. The products of reduction of the two carbinols were found to be identical. The compound proved to be 3-hydroxy-1-phenylbutane, $C_6H_5-CH_2-CH_2-CH(OH)-CH_3$, which was identified by means of its boiling point, 105° under 6 mm. pressure, and the melting point of its phenylurethan, 114°. The identity of the reduction products of the two carbinols was definitely established by comparing the melting points of their phenylurethans.

3-Hydroxy-1-phenylbutane has been prepared before by the reduction with sodium amalgam of benzalacetone⁶ and of benzylacetone.⁷ Since alkaline reagents are known to cause rearrangements of such compounds, we synthesized the 3-hydroxy-1-phenylbutane by the condensation of hydrocinnamic aldehyde with methylmagnesium bromide. The 3-hydroxy-1-phenylbutane prepared in this way was identical with that reported in the literature.

The relative rates of catalytic hydrogenation of the two carbinols were determined. An apparatus designed by Muskat and Knapp⁸ for the study of the rates of catalytic hydrogenation of unsaturated compounds was used. The apparatus was so designed that the pressure of the hydrogen always remained constant while the volume of the hydrogen varied. Under the same experimental conditions and with equal weights of catalyst from the same batch, the *cis* carbinol was hydrogenated more rapidly than was the *trans* carbinol. This is in perfect agreement with the work of Paal,⁹ who has shown, after a detailed study of a large number of geometric isomers, that the *cis* compound is always more rapidly hydrogenated than is the corresponding *trans* isomer. Complete experimental data and graphs for the hydrogenation of each of the carbinols will be given in the Experimental Part.

The oxidation of the two carbinols with perbenzoic acid was studied. It was found that under the same experimental conditions the *cis* carbinol

⁵ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, pp. 10, 92.

⁶ Engler and Leist, *Ber.*, 6, 255 (1873).

⁷ Klages, *ibid.*, 37, 2313 (1904).

⁸ To be published soon.

⁹ Paal, *Ber.*, 60, 1221 (1927); *ibid.*, 63, 766 (1930).

was oxidized more rapidly than was the *trans* carbinol. This same difference was also observed in the rate of oxidation with perbenzoic acid of the two geometric isomers of phenylbutadiene.⁸ This suggests that it might be possible to use the relative rates of oxidation with perbenzoic acid as a means of distinguishing between geometric isomers.

Both Böeseken¹⁰ and Meerwein¹¹ have attempted to calculate the velocity constants for the oxidation of unsaturated compounds by means of perbenzoic acid. They have concluded from their results that the oxidation follows a second order reaction. These conclusions seem to us to be not wholly warranted since the data show a decided decrease in the second order reaction constant as the oxidation proceeds. Thus, for the oxidation of pinene, Meerwein has calculated the following values for the second order reaction constant K

Minutes	5	10	20	40	60
$K \times 10^3$	1573	1138	985	866	845

It appears to us that these oxidation reactions are not properly expressed by the equation for a second order reaction.

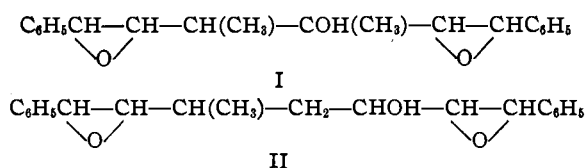
We have calculated the velocity constants for the oxidation experiments reported here. After calculating K for a first, second and third order reaction, it became quite obvious that the oxidation of methylstyryl-carbinol is best expressed by the equation for a third order reaction. K_3 is remarkably constant for this type of work and is well within the experimental limits of error.

The exact significance that may be attached to this is still uncertain. It seems that the rate of oxidation of an unsaturated compound with perbenzoic acid is proportional to the concentration of the unsaturated compound and to the square of the concentration of the perbenzoic acid. Further work on the oxidation of unsaturated compounds by means of perbenzoic acid and also of peracetic acid is contemplated.

The oxides of each of the carbinols were isolated. They had approximately the same boiling points: the oxide of the *trans* carbinol distilled at 118° under 4 mm. pressure, while the oxide of the *cis* carbinol distilled at 117° under 3.5 mm. pressure. The oxide of the *trans* carbinol was prepared in larger quantity in order to study its chemical properties. A number of attempts were made to break the oxide linkage but with no success. It was heated for several hours with 2 *N* sulfuric acid, and in place of the expected trihydroxyphenylbutane a condensation product was obtained which was formed by the elimination of one mole of water from two moles of the oxide of the *trans* carbinol. The condensation product distilled at 200° under 4-mm. pressure. It may have either of the following two structures (the geometric isomerism will not be indicated).

¹⁰ Böeseken, *Rec. trav. chim.*, **44**, 90 (1925).

¹¹ Meerwein, *J. prakt. Chem.*, **113**, 24 (1926).



For the same reasons given above for the condensation product of the *trans* carbinol, we favor Structure I. The same condensation product was obtained on heating the oxide with dilute sulfuric acid in a bomb tube for several hours at 150°.

Dry hydrogen chloride was passed into an ethereal solution of the oxide of the *trans* carbinol. The hydroxyl group of the carbinol was attacked but the oxide linkage remained intact.

The oxide of the carbinol was heated for several hours with dilute alkali. No reaction occurred and the original oxide was isolated.

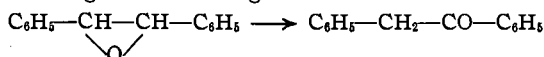
Dry ammonia gas was bubbled through an alcoholic solution of the oxide for several hours but no reaction occurred.

This remarkable stability of the oxide linkage casts some doubt as to the presence of such a linkage in the molecule. It may be that the oxide had rearranged to a ketone in a manner normal to ethylene oxides.



It is interesting to note that different samples of the pure oxide always gave typical ketonic color reactions but every effort to prepare a derivative of such a ketone failed.

The oxide of stilbene has been found to show very much the same stability as does the oxide of the *trans* carbinol. However, the oxide of stilbene could not have undergone a rearrangement to the ketone



desoxybenzoin, for the properties of the two are decidedly different.

An effort was made to oxidize the methylstyrylcarbinols with potassium chlorate and osmic acid but with no success.

Experimental Part

The two methylstyrylcarbinols were prepared according to the method described in the preceding article by Muskat and Herrman.¹

I. Reactions of the Hydroxyl Group

(a) *Phenylurethan*.—The phenylurethan of the *trans* methylstyrylcarbinol was prepared as follows. Equimolar quantities of the carbinol and of phenyl isocyanate, each dissolved in a small amount of dry ligroin, were mixed together and the solution was allowed to stand. In a few hours an oily layer settled out and crystals slowly formed in the oil. After several days the oil was completely transformed into a yellowish crystalline mass. The ligroin was poured off and the crystals were dissolved in hot benzene. After filtration the benzene was removed by vaporization. The light yellow

crystalline deposit which remained was purified by several recrystallizations from hot alcohol. The pure, white crystals melted at 94°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.36; H, 6.41; N, 5.24. Found: C, 76.42, 76.45; H, 6.74, 6.68; N, 5.29, 5.29.

If the *cis* carbinol is treated in a similar manner with phenyl isocyanate, water is eliminated, and the phenyl isocyanate is converted to the crystalline carbanilide, m. p. 235°, which is insoluble in benzene. No trace of a phenylurethan could be detected.

(b) *Acetate*.—The acetate of the *trans* carbinol was prepared according to Burton's⁸ method, by refluxing 10 g. of the carbinol with 15 cc. of acetic anhydride for six hours. An acetate which distilled at 141–144° under 15 mm. pressure, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.67, 75.25; H, 7.61, 7.57.

It appears from these results that Burton had the *trans* carbinol but was not aware of it.

Under the same conditions the *cis* carbinol is dehydrated to give a preponderance of the dimer of phenylbutadiene. This was proved by analysis of the product.

(c) *Chloride*.—The *trans* carbinol was dissolved in approximately twice its volume of anhydrous ether, and dry hydrogen chloride was allowed to pass in until it ceased to be absorbed. The flask was immersed in an ice-bath during the reaction. The ethereal solution was then thoroughly washed with water to remove all of the 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 104° under 6 mm. pressure.

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

Under the same conditions the *cis* carbinol reacted with hydrogen chloride to give an almost quantitative yield of a chloride which distilled at 108° under 6 mm. pressure.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.29, 21.43.

It should be emphasized that for the preparation of either of the chlorides it is essential to remove all traces of acid before distillation. If any acid remains the chlorides decompose on distillation to give a tarry residue.

The *trans* chloride was refluxed with a 10% solution of sodium acetate. The reaction mixture was then extracted with ether, the ethereal solution dried over anhydrous sodium sulfate, and the ether removed by vaporization. The residual oil was distilled under diminished pressure. Two fractions were collected: (1) b. p. 118° under 4 mm. pressure, (2) b. p. 200° under 6 mm. pressure. These fractions were analyzed: (1) proved to be the acetate of the *trans* carbinol which was described above, while (2) was a condensation product of the *trans* carbinol which will be described later in the paper.

The *trans* chloride was refluxed with a water suspension of silver oxide until all of the chloride had reacted. The reaction mixture was then extracted with ether and worked up in the usual manner as described above. Two fractions were collected: (1) b. p. 76° under 11 mm. pressure and (2) b. p. 194° under 3 mm. pressure. Fraction 1, of which but a small amount was obtained, proved to be the *trans* phenylbutadiene, while fraction (2) was the polymer of the *trans* phenylbutadiene. These compounds were identified by analyses.

The *trans* chloride was refluxed with about five times its volume of dry pyridine for several hours. The reaction mixture was then taken up in ether, and the ethereal solution was thoroughly washed with water to remove all of 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,

with the exception of a small fraction, distilled over completely at 76° under 11 mm. pressure, the boiling point of the *trans* phenylbutadiene. It was further identified by analysis.

The *cis* chloride was treated with pyridine in an analogous manner and yielded about 40% of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure. The remainder was polymerized to the dimer, b. p. 205° under 10 mm. pressure. Both compounds were further identified by analyses.

The *trans* chloride was shaken with twice the theoretical amount of 5% sodium hydroxide for approximately twenty-four hours. The mixture was then extracted with ether, the ethereal solution thoroughly washed with water to remove the excess alkali, dried over anhydrous sodium sulfate, and the ether was removed by vaporization. The residual oil distilled almost completely at 76° under 11 mm. pressure, which is the boiling point of the *trans* phenylbutadiene.

When treated with alkali under the same conditions, the *cis* carbinol gave a very small yield of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure, and the remainder was polymerized to the dimer. Both compounds were further identified by analyses.

(d) **Condensation.**—The *trans* methylstyrylcarbinol was heated to a temperature of 180° under atmospheric pressure. Droplets of water were formed on the sides of the reaction vessel and the mass became viscous and assumed a dark brown color. The viscous mass was extracted with ether, the ethereal solution dried over sodium sulfate, and the ether was removed by vaporization. The residual oil was distilled under diminished pressure. After a small amount of unchanged carbinol distilled over, the temperature rose quickly to 200° , at which point the bulk of the material distilled over under 6 mm. pressure.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.27; H, 7.97. Found: C, 86.38, 86.17; H, 8.18, 7.76. Calcd. for $C_{20}H_{22}O$: mol. wt., 278.17. Found: mol. wt., 282.3.

The condensation product was ozonized in a manner entirely analogous to that described for the *trans* methylstyrylcarbinol in the preceding paper.¹ Five grams of the condensation product gave 2.3 g. of the semicarbazone of benzaldehyde and 1.6 g. of benzoic acid. This corresponds to a 76.3% yield of benzaldehyde on the basis of two moles of benzaldehyde for each mole of the condensation product.

A chloroform solution of the condensation product was treated with two moles of bromine, also in chloroform solution. This solution was completely decolorized, but no further absorption followed the addition of a few more drops of bromine solution. The chloroform was removed and the residual solid mass was recrystallized several times from hot ligroin. The pure bromide melted at 179° .

Anal. Calcd. for $C_{20}H_{22}OBr_4$: Br, 53.47. Found: Br, 53.55, 53.35.

II. Reactions Involving the Double Bond

(a) **Bromination.**—A number of attempts to prepare a dibromide addition compound of the two carbinols were made but with no success. In every case decomposition occurred with the elimination of water, resulting in the formation of the tetrabromide of phenylbutadiene. This was identified by its melting point, 146° , and the melting point of a mixture with a sample of known origin. In one experiment the carbinol (in an open weighing bottle) was placed in a desiccator containing an equivalent amount of bromine, also contained in a weighing bottle. The desiccator was closed and the bromine, which vaporized slowly, reacted with the carbinol. Even under such mild conditions, decomposition of the carbinol occurred, with the formation of the tetrabromide of phenylbutadiene.

(b) **Catalytic Hydrogenation.**—Each of the two carbinols was hydrogenated cata-

lytically by the Adams method.⁵ The catalyst was prepared in the manner described by Adams and methyl alcohol was used as the solvent. After the hydrogenation was complete, the catalyst was removed by filtration, and the filtered solution was subjected to distillation under diminished pressure. The methyl alcohol was first removed, after which, in each instance, the temperature rose to 105° under 6 mm. pressure, and the remainder distilled over completely at this temperature.

Anal. Calcd. for C₁₀H₁₄O: C, 79.94; H, 9.4. Found: C, 79.91, 79.79; H, 9.34, 9.76.

The phenylurethan of each of the reduced carbinols was prepared by merely adding an equivalent weight of phenyl isocyanate to the pure reduction products and allowing to stand for a few hours. In each case the solution solidified completely. After several recrystallizations from alcohol, the pure crystals melted at 113°, as did a

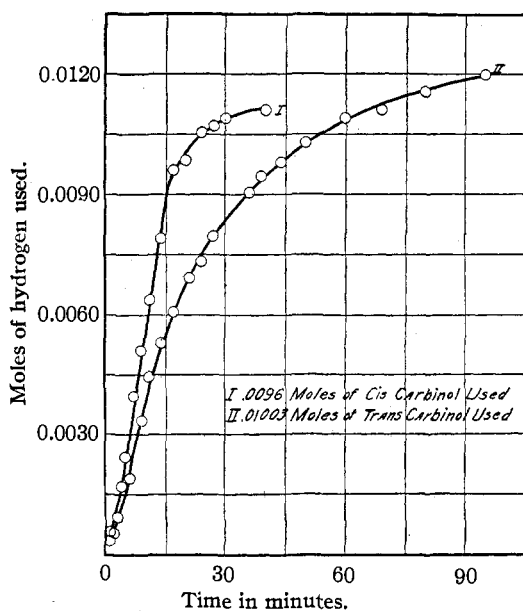


Fig. 1.—50 cc. of glacial acetic acid used as solvent.

determining the rates of catalytic hydrogenation will be described in detail in a paper to be published soon by Muskat and Knapp.

Ten-milligram portions of the same batch of the catalyst were used in all of the experiments. The barometric pressure was 747 mm. and the temperature was 29° except in the case of the *trans* methylstyrylcarbinol in glacial acetic acid, where it was 744 mm. and the temperature 27°. The excess pressure in every case was 88 cm. The experimental data obtained are given graphically in Figs. 1 and 2.

(d) Oxidation of the Methylstyrylcarbinols with Perbenzoic Acid.—Each of the two isomeric carbinols was oxidized with perbenzoic acid. The perbenzoic acid was prepared according to the method of Tiffeneau.¹² The carbinols, dissolved in chloroform, were treated with a chloroform solution of perbenzoic acid following the method

¹² "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 30.

mixture of the two. This proved the identity of the reduction products of the two carbinols.

The 3-hydroxy-1-phenylbutane was synthesized by condensing hydrocinnamic aldehyde with methylmagnesium bromide and decomposing the resulting addition compound with dilute acid, in a manner entirely analogous to that described by Muskat and Herrman¹ for the preparation of the *trans* carbinol. The 3-hydroxy-1-phenylbutane, prepared in this manner, also distilled at 105° under 6 mm. pressure, and gave a phenylurethan which melted at 113° and did not lower the melting point of the above phenyl urethans when mixed with it.

(c) The Relative Rate of Catalytic Hydrogenation of the Two Isomeric Carbinols.—The apparatus and method used in

first used by Prileshajew¹³ for the oxidation of unsaturated compounds. The rate of oxidation was easily followed by the usual iodimetric titration. The rates of oxidation of the two carbinols were determined at different temperatures and with different concentrations of perbenzoic acid. A blank on the perbenzoic acid was always run concurrently with each of the oxidation experiments. Only those runs are included here in which the blank was negligible. At definite time intervals 2 cc. of the solution was removed, added to an acidified solution of potassium iodide, and the liberated iodine was titrated with standard sodium thiosulfate solution.

Previous investigators, who determined the rate of oxidation of unsaturated compounds by means of perbenzoic acid, have experienced considerable difficulty in obtaining reproducible results. Thus Böeseken and Blumberger¹⁴ state that some unknown catalytic effect influenced the rate of oxidation. They state further that oxidation occurs more readily with perbenzoic acid that has been allowed to age than with freshly prepared perbenzoic acid. Meerwein,¹⁵ on the other hand, reports directly conflicting results. During our study of the rate of oxidation of the two carbinols we were able to prove conclusively that the inconsistent results first obtained were not due, in this particular case, to any variation in the perbenzoic acid but rather to the method of titration. When the sample (2 cc.) that was taken out for titration was added to the dilute acetic acid solution of potassium iodide, iodine was set free. If this mixture is allowed to stand before titration, the iodine is absorbed by the unsaturated compound and a much lower titer is obtained. For unsaturated compounds that are but slowly oxidized, such a lowering of the titer may easily change the data by 100%. Consequently in all of the data given here the iodine that was set free was immediately titrated. If this precaution was taken it was easily possible to duplicate our results. The graphs for the oxidation of the two isomeric methylstyryl carbinols are given in Fig. 3.

We have calculated the velocity constants for the oxidation experiments reported here. Since the initial molar concentrations of the perbenzoic acid and of the carbinols were very nearly equal, we were able to use the following set of equations for the determination of the velocity constants.

$$\text{First order: } K_1 = \frac{2.303}{t} \log \frac{A}{A-x}$$

¹³ Prileshajew, *Ber.*, **42**, 4811 (1909). See also Nametkin and Brusoff, *J. prakt. Chem.*, **112**, 169 (1926); Meerwein, *ibid.*, **113**, 9 (1926); Böeseken, *Rec. trav. chim.*, **47**, 683 (1928); *ibid.*, **48**, 363 (1929).

¹⁴ Böeseken and Blumberger, *ibid.*, **44**, 90 (1925).

¹⁵ Meerwein, *J. prakt. Chem.*, **113**, 24 (1926).

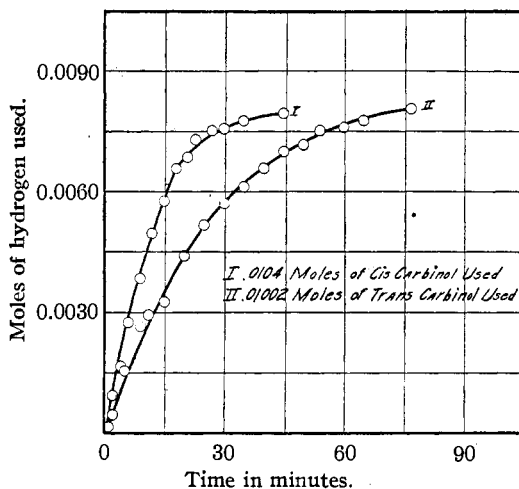


Fig. 2.—50 cc. of CH₃OH used as solvent.

$$\text{Second order: } K_2 = \frac{1}{t} \frac{1}{(A-x)} - \frac{1}{A}$$

$$\text{Third order: } K_3 = \frac{1}{2t} \frac{1}{(A-x)^2} - \frac{1}{A^2}$$

A is initial concentration of perbenzoic acid and of the carbinol; $(A-x)$ is concentration of perbenzoic acid at time t .

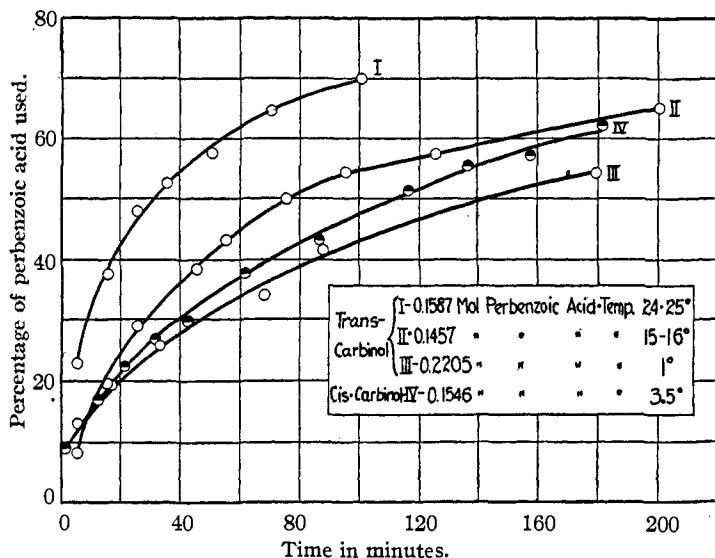


Fig. 3.

Trans Methylstyrylcarbinol, I.—Twenty-two grams of sample; total volume of solution, 950 cc.; temp., 24–25°; $\text{Na}_2\text{S}_2\text{O}_8$, 0.1100 *N*.

$$A = 0.1587 \text{ mole per liter. } (A-x) = 0.0275 \times \text{cc. of } \text{Na}_2\text{S}_2\text{O}_8$$

Minutes	0	5	15	25	35	50	70	100
$\text{Na}_2\text{S}_2\text{O}_8$, cc.	5.77	4.68	3.65	3.00	2.75	2.44	2.07	1.81
K_1	..	0.042	0.031	0.026	0.021	0.017	0.015	0.012
K_2	..	0.294	0.245	0.233	0.198	1.61	0.72	0.138
K_3	..	2.07	2.00	2.14	1.94	1.82	1.93	1.82

$$K_3 \text{ (average)} = 1.96 \text{ Average deviation, 4.8\%}$$

Trans Methylstyrylcarbinol, II.—Seventeen grams of sample; total volume of solution, 800 cc.; temp., 15–16°; $\text{Na}_2\text{S}_2\text{O}_8$, 0.1100 *N*.

$$A = 0.1457 \text{ mole per liter. } (A-x) = 0.0275 \times \text{cc. of } \text{Na}_2\text{S}_2\text{O}_8$$

Minutes	0	5	15	25	45	55	75	95	125	200
$\text{Na}_2\text{S}_2\text{O}_8$, cc.	5.30	4.85	4.25	3.75	3.25	3.00	2.65	2.50	2.25	1.85
K_1	..	0.0176	0.0147	0.0138	0.0109	0.0104	0.0092	0.0087	0.0069	0.0053
K_2	..	0.127	0.113	0.113	0.096	0.096	0.091	0.0807	0.074	0.064
K_3	..	0.909	0.869	0.939	0.867	0.907	0.940	0.865	0.856	0.848

$$K_3 \text{ (average)} = 0.889. \text{ Average deviation, 3.5\%}$$

Trans Methylstyrylcarbinol, III.—Thirty grams of sample; total volume of solution, 970 cc.; temp., 1°; Na₂S₂O₃, 0.1100 *N*.

$A = 0.2205$ mole per liter. $(A - x) = 0.0275 \times \text{cc. of Na}_2\text{S}_2\text{O}_3$

Minutes	0	16.5	32.5	67.5	87.5	179
Na ₂ S ₂ O ₃ , cc.	8.02	6.53	5.93	5.26	4.59	3.65
K_3	..	[0.316]	0.262	0.202	0.241	0.219

K_3 (average) = 0.231. Average deviation, 8.9%

Cis Methylstyrylcarbinol, IV.—Eighteen and three-tenths grams of sample; total volume of solution, 800 cc.; temp., 3.5°; Na₂S₂O₃, 0.1014 *N*.

$A = 0.1546$ mole per liter. $(A - x) = 0.02535 \times \text{cc. of Na}_2\text{S}_2\text{O}_3$

Minutes	0	21	31	42	61	86	116	136	157
Na ₂ S ₂ O ₃ , cc.	6.10	4.75	4.45	4.28	3.80	3.45	2.95	2.70	2.60
K_3	..	0.642	0.593	0.513	0.540	0.516	0.590	0.631	0.599

K_3 (average) = 0.578. Average deviation, 7.14%.

Summary

1. The chemical reactions of the two geometric isomers of methylstyrylcarbinol were studied. These studies included the reactions involving the hydroxyl group and the double bond. The differences in the reactivity of the two carbinols were noted in each case.

2. The relative rates of catalytic hydrogenation of the two isomeric carbinols were determined. The *cis* carbinol was reduced more rapidly than the corresponding *trans* carbinol.

3. The relative rates of oxidation of the two isomeric carbinols by means of perbenzoic acid were determined. The *cis* carbinol was oxidized more rapidly than the corresponding *trans* carbinol.

4. The velocity constants for these oxidation reactions were calculated and it was found that the rate of oxidation of the two carbinols is best expressed by the equation for a third order reaction.

5. The oxides of the two carbinols were prepared and their reactions studied.

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