

outgassed and reduced by hydrogen, and subsequently outgassed; a few measurements were made on the degreased, outgassed surface. The surface was more readily conditioned to reproducibility of the sorption within the error of measurement than for mild steel.

Neon and hydrogen are not measurably sorbed in the range of temperature and pressure studied. Argon is very slightly sorbed at -183° and cannot be removed by pumping at temperature; the magnitude of the sorption is about the same as that of strongly held carbon dioxide at -78° . Nitrogen is sorbed to a greater extent at -183° , sufficient at apparent saturation to cover about one-half of the measured geometric surface and the sorption is completely reversible.

Carbon monoxide is the only gas which is physically adsorbed to as great an extent as a complete monolayer; furthermore the reversible sorption of this gas confirms the measured geometric area of the surface. Hence, it is concluded that at the low pressures used in this work only the reversible sorption of carbon monoxide at -183° is a

reasonably reliable criterion of surface area in the case of stainless alloys whereas on mild steels nitrogen and argon are also satisfactory.

The agreement of the sorption data for the two alloys indicates that the surfaces are of the same specific area and this appears to approximate unity.

There is evidence of a tendency to form a second adsorbed layer in the case of Alloy B. Sorption data for Alloy B also show more marked deviation from the Langmuir equation in the lowest pressure region. These observations suggest that the surface of Alloy B is in a more reduced condition than that of Alloy A. Furthermore the proportionally greater chemisorption of carbon monoxide at -183° on Alloy B leads to the conclusion that there is more free metal on this surface.

The sorption of oxygen at -183° consists of a fraction of a monolayer reversibly held and about two monolayers which are chemisorbed. At -78 and 20° three and four layers, respectively, of oxygen are chemisorbed.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. V.¹ The Effect of Cyclohexene upon the Isomerization of Methylcyclopentane and Cyclohexane

BY HERMAN PINES, B. M. ABRAHAM² AND V. N. IPATIEFF

It was shown previously^{1,3} that under certain carefully controlled conditions aluminum bromide-hydrogen bromide or aluminum chloride-hydrogen chloride did not cause the isomerization of *n*-butane to isobutane unless traces of olefins were present. This study has now been extended to the investigation of the reversible isomerization of methylcyclopentane to cyclohexane using aluminum bromide-hydrogen bromide as the catalyst. A high vacuum technique was used for the purification of materials, and for charging and discharging of the products.

It was found that methylcyclopentane did not undergo isomerization when shaken in a sealed tube for nineteen hours at 25° in the presence of as much as 9 mole per cent. of aluminum bromide⁴ and 1 mole per cent. of hydrogen bromide. When the hydrogen bromide concentration was increased to 3.2 mole per cent., the yield of cyclohexane produced was 2%. However, when 0.05 mole per cent. of olefin such as cyclohexene was added to the


reaction mixture, 28 mole per cent. of the methylcyclopentane was converted to cyclohexane. By increasing the molal ratio of the cyclohexene from 0.05 to 0.07 and to 0.1 mole per cent. the amount of cyclohexane formed increased to 30 to 38 mole per cent., respectively. The results are summarized in Table I. The amount of methylcyclopentane listed in the above table and in subsequent experiments was 8.00 to 10.00 g. \pm 0.001 g.

TABLE I

THE EFFECT OF OLEFINS ON ISOMERIZATION

Reaction time 19 hrs. The amount of methylcyclopentane used in the various experiments varied from 8-10 g.

Reagents: moles/100 moles methylcyclopentane

No.	AlBr ₃	HBr		Analysis mole % cyclohexane
1	1.0	1.0	0.0	0
2	9.0	1.0	.0	0
3	9.0	3.2	.0	2
4	9.0	1.0	.05	28
5	9.0	1.1	.07	30
6	9.0	1.0	.10	38
7	1.0	1.0	.20	58

A 58% yield of cyclohexane was obtained when the concentration of cyclohexene added was 0.2 mole per cent.; in this particular experiment the

(1) The previous paper of this series was marked as "Isomerization of Alkanes. IV," see H. Pines and R. C. Wackher, *THIS JOURNAL*, **68**, 2518 (1946).

(2) Universal Oil Products Company Postdoctoral Fellow 1946-1947. Present address Argonne National Laboratory, Chicago, Illinois.

(3) H. Pines and R. C. Wackher, *THIS JOURNAL*, **68**, 595 (1946).

(4) Throughout this paper for the purpose of calculation the aluminum bromide was considered to be monomeric.


concentration of aluminum bromide was 1 mole per cent. instead of the usual 9 mole per cent. In the absence of hydrogen bromide, aluminum bromide does not isomerize methylcyclopentane even in the presence of olefins.

Cyclohexene reacted in the presence of an aluminum bromide-hydrogen bromide catalyst in a manner similar to methylcyclopentane. Isomerization did not occur when a solution consisting of 100 mole per cent. of cyclohexane was treated for nineteen hours at $25 \pm 0.1^\circ$ with 2.00 mole per cent. of aluminum bromide and 0.99 mole per cent. of hydrogen bromide. In the presence, however, of 0.107 mole per cent. of cyclohexene, 9% of cyclohexane isomerized to methylcyclopentane.

In order to determine the effect of the different variables upon the degree of isomerization of methylcyclopentane, the effect of hydrogen bromide and aluminum bromide concentration was investigated.

By maintaining the molal ratio of methylcyclopentane to aluminum bromide and to cyclohexene (cyclohexyl bromide) constant at about 100:9.0:0.08 and by varying the concentration of hydrogen bromide a definite trend in the degree of isomerization was observed. This effect was most pronounced when the concentration of hydrogen bromide was raised from 1.1 to 3 mole per cent.; in this case the degree of isomerization increased from 30 to 78%. Under similar conditions but in the absence of hydrogen bromide and cyclohexyl bromide no isomerization of methylcyclopentane was observed; this definitely establishes that the initiator is the alkyl halide or its equivalent. The results are summarized in Table II.

TABLE II
THE EFFECT OF HBr CONCENTRATION ON ISOMERIZATION
Reagents: moles/100
moles hydrocarbon


No.	Reaction time, hours	AlBr ₃	HBr		Analysis mole % cyclohexane
8	19	9.1		0.08 ^a	17
9	19	8.9	0.02	.08 ^a	25
10	19	9.1	0.28	.08	20
11	19	9.0	1.1	.07	30
12	19	9.1	3.0	.08	78
13	1	1.6	1.0	.1	19
14	1	1.0	3.1	.1	36
15	1	1.0	1.0	.1 ^a	21
16	1	1.0	0	.1	0

^a Olefin added as cyclohexyl bromide.

An increase in the isomerization of methylcyclopentane with an increase of hydrogen bromide concentration was also noticed when the aluminum bromide was maintained at lower concentrations and the contact time was one hour instead of the usual nineteen hours.

It was found that by decreasing the aluminum bromide concentration from 9 to 1 mole per cent.

TABLE III
THE EXTENT OF ISOMERIZATION WITH TIME
Reagents: moles/100
moles hydrocarbon

No.	Reaction time, hours	AlBr ₃	HBr		Analysis mole % cyclohexane
17	0.5	1.0	1.0	0.10	12
18	1.0	1.0	1.0	.10	21
13	1.0	1.6	1.0	.10	19
19	1.25	9.0	0.9	.10	23
20	2.0	2.0	1.0	.10	34
21	19	1.0	1.1	.10	40
6	19	9.0	1.1	.10	38


based on methylcyclopentane present and maintaining the molal concentration of hydrogen bromide at 1 and of cyclohexene at 0.1 mole per cent., the degree of isomerization within the experimental error was unchanged (Table III, Experiments 6 and 21). These results show that even 1 mole per cent. of aluminum bromide under the experimental conditions used seems to be in excess of that required to catalyze the isomerization. At about 9 mole per cent. concentration aluminum bromide is near the saturation point at 25° .

The isomerization catalyst comprised of aluminum bromide-hydrogen bromide and promoted by cyclohexene loses its activity with time. This was shown in Experiment 22 (Table IV) in which methylcyclopentane was treated by this catalyst for a period of nineteen hours; a sample was then withdrawn for analysis and the contents of the reaction tube were diluted with an equal volume of methylcyclopentane; the tube was agitated for an additional nineteen hours at 25° . It was found that no additional isomerization occurred. These results suggested that the isomerization reaction must have stopped before the first nineteen-hour period was ended. This was shown more clearly in Experiment 20 (Table IV) in which the reaction was carried out for only two hours; the hydrocarbons were then withdrawn and the reaction tube was recharged with fresh methylcyclopentane and with the recovered hydrogen bromide. The tube was then agitated for two hours at 25° . From the results obtained it is seen that the reaction was almost complete during the first two hours.

On the basis of the above-described experiments it was believed that the loss of the catalyst activity was due primarily to the disappearance of the promoter through secondary reactions. This was demonstrated more clearly in Experiment 23 in which methylcyclopentane was treated with aluminum bromide-hydrogen bromide promoted by 0.11% of cyclohexene. After nineteen hours a small sample was withdrawn for analysis; it contained 38% of cyclohexane. In order to be certain that the catalyst had lost its activity, the reaction tube was resealed and shaken in the constant temperature bath for an additional nineteen

TABLE IV

THE STUDY OF CATALYTIC ACTIVITY AS A FUNCTION OF TIME AND INITIATOR: THE CHANGE IN CATALYST ACTIVITY WITH

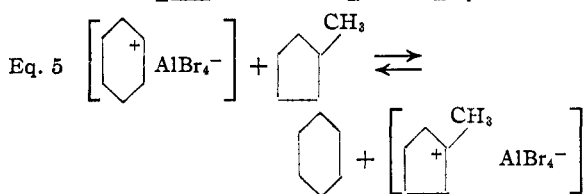
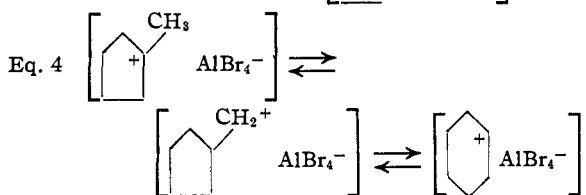
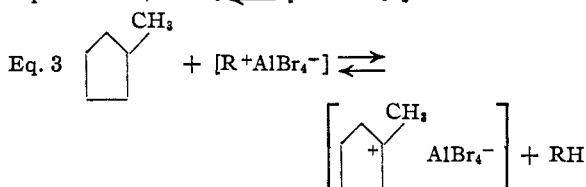
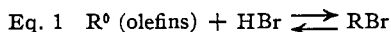
Expt.	TIME		Reagents: initial charge, moles/100 mole of methylcyclopentane		Analysis, mole % cyclohexane	Reaction time, hours	Second charge, moles hydrocarbon Second period	Analyses mole % cyclohexane
	Reaction time, hours	AlBr ₃	First period					
			HBr					
22	19	2.0	0.9	0.09	28	19	93 ^a	14
20	2	2.0	1.0	.10	34	2	100 ^b	9
23	19	1.0	1.0	.11	38 ^c	19	0.12 ^d	80

^a Removed equivalent of 7 moles for analysis; diluted with an equivalent of 93 moles of methylcyclopentane. ^b Replaced first batch of hydrocarbon. The hydrocarbons from the first period of reaction were removed and replaced with 100 mole equivalent of fresh methylcyclopentane. ^c The reaction was continued for an additional nineteen hours between first and second period. No additional isomerization occurred. ^d Cyclohexene was added to the reaction mixture.

hours and then retested; it was found that no further isomerization occurred. The introduction, however, of 0.12% of cyclohexene restored and increased the activity of the catalyst; the reaction mixture after this treatment consisted of 80% cyclohexane.

Discussion of Results

The experimental data given above indicate that under controlled conditions methylcyclopentane does not undergo isomerization in the presence of aluminum bromide-hydrogen bromide catalyst unless traces of cyclohexene or cyclohexyl bromide are present. These results are in accordance with a similar observation made when isomerizing *n*-butane³ and can be explained by the following chain mechanism similar to that suggested for *n*-butane.⁵



Although the addition of small amounts of cyclohexene or cyclohexyl bromide causes the isomerization to proceed, in no case was an equi-

librium mixture of methylcyclopentane and cyclohexane obtained,⁶ this is probably due to a chain-breaking reaction in which the carbonium ion of either of the original additives is involved or the one formed through a hydrogen transfer reaction as exemplified by Equation 3. The chain-breaking can be caused by such reactions as conjunct polymerization,⁷ cycloalkylation, or condensation which involves a transfer of hydrogen.⁸ The conjunct polymerization involves the transformation of the olefins into saturated hydrocarbons of the same or higher molecular weight and the formation of highly unsaturated hydrocarbons which form a complex with the catalyst which is insoluble in hydrocarbons. This might explain the formation of an oily film during isomerization which can be detected on the walls of the reaction tube. The conjunct polymerization is probably one of the chief reactions causing the destruction of the carbonium ions; this reaction is relatively rapid and pronounced when the concentration of the olefins is relatively high. For that reason, in order to obtain the most benefit from the olefins added, it is preferred that the olefins be not added at once but at intervals and in small quantities. This is brought up in Table IV.

Experimental

A high vacuum apparatus similar to that reported previously³ was constructed (Fig. 1); all liquid reactants once purified in this apparatus were kept out of contact with air or moisture.

The aluminum bromide was a resublimed commercial grade which was further purified by a vacuum sublimation through a series of constrictions into a receiver. This receiver contained several weighed and numbered capsules. To fill these capsules the following procedure was adopted: A few millimeters pressure of dry air was admitted to the line and the aluminum bromide was heated to the melting point; as soon as the salt became molten an atmosphere of dry gas was admitted thus forcing the molten salt into the capsule. After the material had solidified the capsules were removed from the line, sealed and reweighed. Each capsule contained from 1.7–2.2 g. of aluminum bromide. In Fig. 2 is illustrated the reaction tube with an aluminum bromide capsule in place.

(6) The equilibrium mixture at 25° consists of 88% of methylcyclopentane and 12% of cyclohexane.

(7) V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**, 464 (1946).

(8) H. Pines and V. N. Ipatieff, *ibid.*, **6**, 242 (1941); *THIS JOURNAL*, **70**, 531 (1948).

(5) H. S. Bloch, H. Pines and L. Schmerling, *THIS JOURNAL*, **68**, 153 (1946).

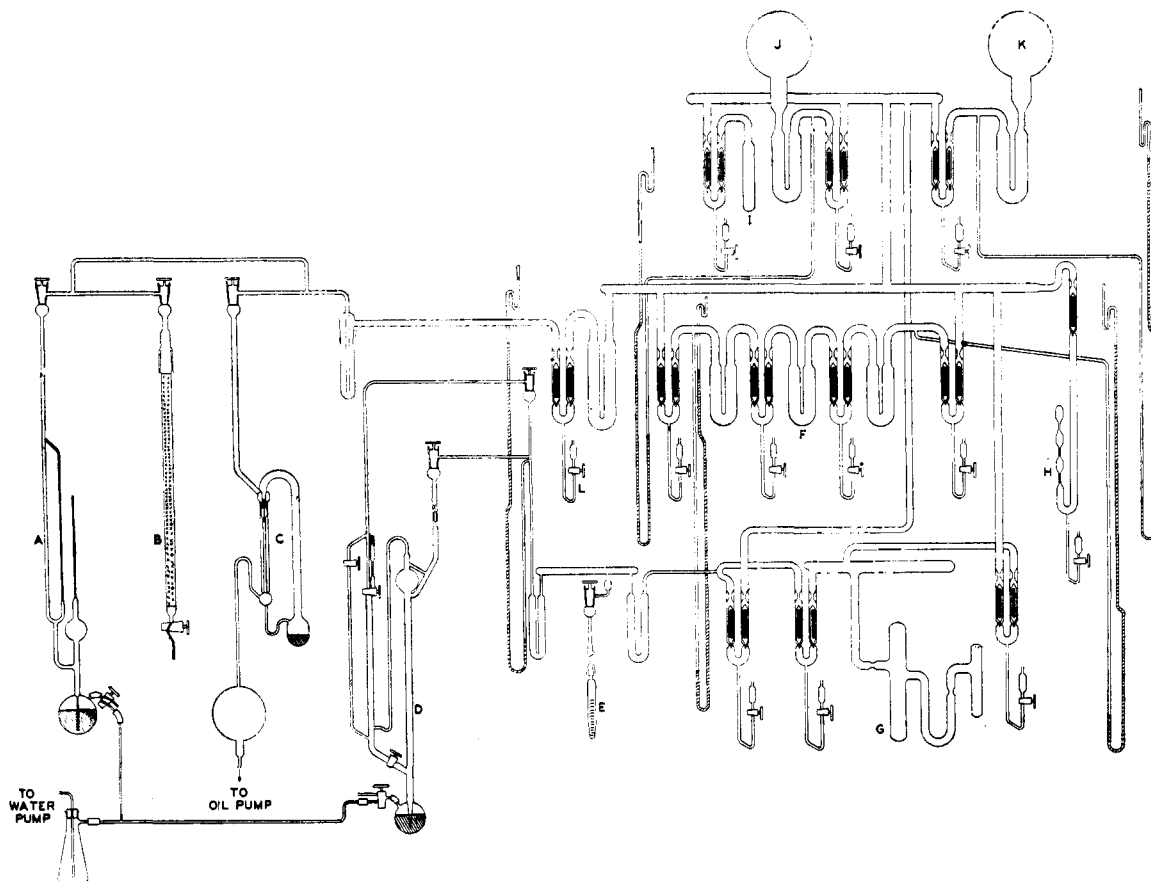


Fig. 1.—Isomerization apparatus: A, McLeod gage; B, phosphorus pentoxide drying tower; C, mercury diffusion pump; D, Toeppler pump; E, sample inlet; F, fractionation system; G, reaction tube; H, small volume aliquoting tube; I, cyclohexene storage; J, gaseous olefins storage; K, hydrogen bromide storage; L, stock valve.

The methylcyclopentane used in this work was prepared from cyclohexane by catalytic isomerization; this was accomplished by refluxing the cyclohexane in the

presence of aluminum chloride activated by the addition of about 2-3% of water. The methylcyclopentane thus formed, boiling lower than its isomer, was continuously removed on a 50-plate column. The distillate which contained 85-90% methylcyclopentane was washed with alkali, dried, and redistilled on a 100-plate column. The methylcyclopentane fraction used in these experiments did not show any impurities as determined by index of refraction, n_D^{20} 1.4100, or by infrared or ultraviolet spectroscopy. The methylcyclopentane thus obtained was weighed out to give the proper molal ratio for a given aluminum bromide capsule. The liquid was then distilled into a numbered tube which contained liquid sodium-potassium alloy and stored until used (Fig. 3).

The cyclohexene was stored *in vacuo* over sodium-potassium alloy and removed as needed. The olefin was measured as a gas in one of the calibrated U tubes on the apparatus (Section F, Fig. 1).

Hydrogen bromide was prepared by dropping bromine on tetralin. The material was fractionated on the line, discarding generous first and last fractions. The middle fraction which had a dry-ice-ether vapor tension of 400

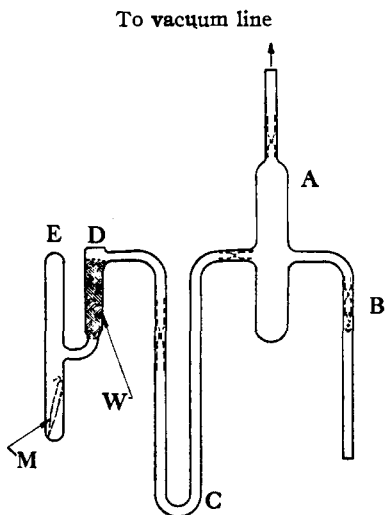


Fig. 2.—Reaction tube: W, glass wool; M, aluminum bromide.

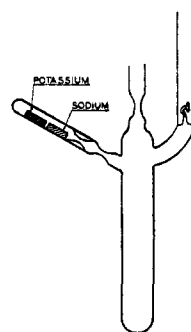


Fig. 3.—Hydrocarbon purification tube.

mm. ("International Critical Tables" value 401 mm.) was stored in a 5-liter bulb (Section K, Fig. 1).

The experimental technique used was as follows: A reaction tube (Fig. 2) was sealed on the line (Section G, Fig. 1), evacuated and degassed. Dry air was then admitted through a phosphorus pentoxide drying column and a small hole was blown in the side tube (Section E, Fig. 2). An aluminum bromide capsule was then dropped into the side-arm after the tip had been broken. The hole was sealed and the tube re-evacuated. When the pressure had dropped to *ca.* 10^{-3} mm. of mercury the aluminum bromide was sublimed through the glass wool, into the U-tube (Section C, Fig. 2); Sections E and D were sealed off. The aluminum bromide was then sublimed into the reaction tube proper and Section C was sealed off. In later experiments the glass wool in D was eliminated. The oily film which is put on the glass during fabrication was difficult to remove and seemed to influence the results. The methylcyclopentane was next added, then the olefin, and finally the hydrogen bromide. The reaction tube was sealed off the line at A and warmed to room temperature. The tube was then placed in the constant temperature bath and agitated for the period of the experiment.

If no olefin or alkyl halide had been added the solution was clear; however, if either of these compounds was present in the reaction mixture, droplets of light yellow oil—insoluble in the hydrocarbon—were always noticed to be formed on the glass. When cyclohexyl bromide was used, cyclohexene was mixed with hydrogen bromide in equimolar amounts in a small capsule. The sealed capsule was then placed in the reaction tube. In this case all reagents except cyclohexene were added as previously described. After the aluminum bromide had dissolved in the methylcyclopentane, the tip of the capsule was broken by shaking the reaction tube. Immediately the whole solution became turbid and yellow; in a short while the oil separated on the glass. In the light of the variation in the experimental results mixing is a very serious problem with these rapid reactions.

After the agitation period, the tubes were attached to the line by sealing a ground joint on tube B, Fig. 2, and inserting this joint at E, Fig. 1. The tube was opened by dropping an iron weight enclosed in glass on the break-off in tube B, Fig. 2. The volatile gases were tested for the presence of non-condensables such as hydrogen or methane. In no case was more than 0.04 cc. S. T. P. of gas recovered (*ca.* 0.0001 mole per cent.). The value was determined with the aid of the Toepler pump (Section D, Fig. 1). The hydrogen bromide was difficult to separate quantitatively from methylcyclopentane so no analysis was attempted here. The hydrocarbon was analyzed by index of refraction and infrared spectroscopy. In no case did the infrared analysis reveal the presence of constituents other than cyclohexane and/or methylcyclopentane.

Summary

The reversible isomerization of methylcyclopentane to cyclohexane in the presence of aluminum bromide-hydrogen bromide catalyst has been studied using high vacuum technique. It was found that under certain controlled conditions methylcyclopentane does not undergo isomerization to cyclohexane unless cyclohexene or cyclohexyl bromide in amounts of about 0.05 mole per cent. or higher are present.

The effect of olefins, hydrogen bromide, and aluminum bromide concentrations upon the isomerization of methylcyclopentane has been studied.

A mechanism of isomerization has been proposed.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Synthesis of Syringaldehyde¹

BY IRWIN A. PEARL

In a study of the separation of guaiacyl from syringyl compounds in fractions obtained from lignin oxidations it was necessary to use large amounts of syringaldehyde. A review of the literature revealed numerous reported syntheses of syringaldehyde,²⁻⁸ but yields were all negligible or low, and syringaldehyde has remained more or less of a laboratory curiosity. However, one obvious synthesis of syringaldehyde has been overlooked by other investigators and that is the series of reactions analogous to the synthesis of vanillin from eugenol.

For years vanillin has been manufactured on a

(1) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(2) Graebe and Martz, *Ber.*, **36**, 1031 (1903).

(3) Guyot, *Compt. rend.*, **149**, 788 (1909).

(4) Mauthner, *Ann.*, **395**, 273 (1913).

(5) Späth, *Monatsh.*, **41**, 278 (1920).

(6) Pauly and Strassberger, *Ber.*, **62**, 2277 (1929).

(7) McCord, *THIS JOURNAL*, **53**, 4181 (1931).

(8) Manske, Ledingham and Holmes, *Can. J. Research*, **22B**, 100 (1945).

large scale from eugenol (the chief constituent of oil of cloves and cinnamon leaf oil) by two general methods. In the first, eugenol is treated with alkali to isomerize it to isoeugenol which, in turn, is oxidized to vanillin by some mild oxidizing agent, such as nitrobenzene and alkali. In the second method, eugenol is acetylated to protect the hydroxyl group, and the acetyleneugenol is oxidized by a strong oxidizing agent, such as dichromate and acid or permanganate. The resulting acetylvanillin is then hydrolyzed to vanillin. The present paper describes a synthesis of syringaldehyde analogous to the first of these vanillin syntheses.

Although the syringyl analog of eugenol is not an easily obtained natural product or article of commerce, its preparation from pyrogallol 1,3-dimethyl ether in good yield has been recorded.^{9,10} Pyrogallol 1,3-dimethyl ether is easily prepared by the controlled methylation of pyrogallol according to Krauss and Crede.¹¹

(9) Mauthner, *Ann.*, **414**, 252 (1917).

(10) Hahn and Wassmuth, *Ber.*, **67**, 702 (1934).

(11) Krauss and Crede, *THIS JOURNAL*, **39**, 1433 (1917).