that heating was continued for ten hours. Examination of the steam distillate revealed the presence of some unreacted *p*-chloronitrobenzene and a yellow solid which, after recrystallizations from water, gave a pure white substance melting at 70°. By checking its hydrochloride, this was shown to be *p*-chloroaniline; yield 5–8%.

A solid residue in the steam distillation flask was filtered off from the hot mother liquor. By fractional crystallization from benzene, this residue was separated into two fractions. The first, after recrystallization from ethyl alcohol, gave light orange crystals melting at 186–187°. This was shown to be 4,4'-dichloroazobenzene; a mixed melting point with an authentic sample of that compound causing no depression; yield 15–20%. The second fraction upon recrystallization from chlorobenzene gave yellow plates melting at 111–111.5°. Calculated % N for 2-(*p*-nitroanilino)-ethanol, 15.38; % N found, 15.64.

The filtrate from the steam distillation flask, upon cooling and standing overnight, deposited shiny, golden crystals. These upon recrystallization from chlorobenzene also melted at 111° and proved to be a further yield of the anilino-ethanol: total yield, 15–20%.

Reduction of the Nitro Condensation Products.—Mossy tin and concentrated hydrochloric acid were used and the mixture refluxed for one hour, made strongly alkaline with sodium hydroxide and extracted with ether. Upon evaporation of the ether, the ortho condensation compound yielded pearly white plates melting, after recrystallization from benzene, at 107°. Calculated % N for 2-(*o*-aminoanilino)-ethanol, 18.42; % N found, 18.28. The para compound gave only an unstable product on reduction which rapidly oxidized to a purple resin.

Summary

1. Monoethanolamine condenses directly with *o*- and *p*-chloronitrobenzenes, in the presence of anhydrous sodium carbonate, to form substituted anilino-ethanols.

2. Under similar conditions, *m*-chloronitrobenzene does not condense.

3. Reduction of the chloronitrobenzenes by the alkanolamine is also effected in these reactions.

NEW YORK, N. Y. RECEIVED JUNE 17, 1937

[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 554]

The Isomeric 2-Pentenes[1]

BY HOWARD J. LUCAS AND ARTHUR N. PRATER

The work herein described was undertaken for the purpose of accounting for the properties of the bromopentanes and dibromopentanes which Kharasch and Darkis[2] and Sherrill and coworkers[3] prepared from various samples of 2-pentene by the respective addition of hydrogen bromide and bromine, for it was these properties which Kharasch and Darkis used as a basis for their hypothesis of electronic isomerism of ethylene compounds. For this purpose it was necessary to synthesize *cis*- and *trans*-2-pentene, and to study the behavior of each hydrocarbon with these reagents. Lauer and Stodola[4] have synthesized the *trans*, by a somewhat different procedure, but did not obtain the *cis* isomer. The *trans* isomer herein described is quite pure, for its properties agree well with those observed by Lauer and Stodola, but it is probable that the *cis* is contaminated by some of the *trans* hydrocarbon.

The configurations herein assigned to the isomeric 2-pentenes are based upon those of the 2-butenes, since the former have been synthesized by a series of operations strictly parallel to those previously employed in the case of the latter.[5] Brockway and Cross, by electron diffraction studies, have established the configurations of the 2-butenes.[6] The previously assumed configurations[5] are in agreement. In this synthesis, 2-pentanone,[7] I, was the starting material; the operations involved are

$$\underset{\text{I}}{CH_3CH_2CH_2COCH_3} \xrightarrow{HCN}$$

$$\underset{\text{II}}{CH_3CH_2CH_2C(OH)(CH_3)CN} \longrightarrow$$

$$\underset{\text{III}}{C_2H_5CH_2C(OH)(CH_3)COOH} \xrightarrow{\text{heat}}$$

$$\underset{\text{IV}}{C_2H_5CH{=}C(CH_3)COOH} \xrightarrow{HI}$$

$$\underset{\text{V}}{C_2H_5CHICH(CH_3)COOH} \xrightarrow{Na_2CO_3} \underset{\text{VI}}{C_2H_5CH{=}CHCH_3}$$

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(1) Presented before the San Francisco Meeting of the American Chemical Society, August 21, 1935. Original manuscript received on July 15, 1936.

(2) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

(3) Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929); Sherrill, Baldwin and Haas, *ibid.*, **51**, 3034 (1929).

(4) Lauer and Stodola, *ibid.*, **56**, 1215 (1934).

(5) Young, Dillon and Lucas, *ibid.*, **51**, 2528 (1929).

(6) Brockway and Cross, *ibid.*, **58**, 2407 (1936).

(7) Kindly supplied by the Standard Oil Development Company through the courtesy of H. E. Buc.

TABLE I

PROPERTIES OF PENTENES

	Isomer	Source	B. p., °C. 740 mm.	B. p., °C. 760 mm.	n^{20}_D	F. p., °C.	Investigators
1	*cis*-2-	Synthesis	35.4	36.2[a]	1.3817	−180 to −178[b]	This paper
2	*trans*-2-	Synthesis	35.4	36.2[a]	1.3799	−135 to −136	This paper
3	*trans*-2-	Synthesis	35.7		1.3797		Lauer and Stodola[4]
4	2-	2-Pentanol		36.4	1.3808	−138 ± 2	Norris and Reuter[8]
5	2-	3-Pentanol		36.4	1.3817[c]	−147	Van Risseghem[9]
6	2-	2-Bromopentane		35.85	1.37849		Sherrill and co-workers[3]
7	2-	3-Bromopentane		36.4	1.37965		Sherrill and co-workers[3]
8	2-	2-Bromopentane		35.85	1.37849	−149	Clark and Hollonquist[12]
9	2-	3-Bromopentane		36.40	1.37965	−144	Clark and Hollonquist[12]
10	1-	Synthesis		30.1–.3	1.3736		Wilkinson[10]

[a] Calculated. [b] Vitrification point; would not crystallize. [c] At 17.2°.

TABLE II

PROPERTIES OF DIBROMOPENTANES

Isomer	Source	B. p., °C.	Pressure, mm.	n^{20}_D	d^{20}_4	F. p., °C.	Investigators
2,3-	*cis*-2-Pentene	92.4	50.1	1.5096	1.6817	−44 to −41	This paper
2,3-	*trans*-2-Pentene	91.0	50.1	1.5096	1.6809	−55 to −53	This paper
2,3-	2-Pentanol	180.5	760	1.5098			Norris and Reuter
2,3-	3-Pentanol	60.5–61	14	1.5093[a]		−66	Van Risseghem
2,3-	3-Bromopentane	178.9	760	1.5074			Sherrill
2,3-	2-Bromopentane			1.5074			Sherrill
1,2-	1-Pentene	85	30	1.5090	1.6740		Wilkinson

[a] At 17°.

TABLE III

BROMOPENTANES FROM HYDROGEN BROMIDE AND PENTENES

		Pentene		Bromopentane		Dibromopentane	
	Source	B. p., °C.	n^{20}_D	B. p., °C.	n^{20}_D	n^{20}_D	Investigator
1	Syn. *cis*-2-Pentene	36.2	1.3817	116.5–118.5	1.4425(?)	1.5096	This paper
2	Syn. *trans*-2-Pentene	36.2	1.3799	117.5	1.4435	1.5096	This paper
3	2-Bromopentane	35.85	1.37849	117–118	1.4416	1.5074	Sherrill
4	3-Bromopentane	36.40	1.37965	118–118.5	1.4442	1.5074	Sherrill
5	2-Pentanol	36.15	1.37967	117–118	1.4418		Sherrill
6	3-Pentanol		1.37935		1.4434		Sherrill
7	Irradiated	36.4	1.37956		1.4421		Sherrill

The results can be summarized: (1) the isomeric *cis*- and *trans*-2-pentenes boil at the same temperature, *viz.*, 35.4° (740 mm.), but differ from each other in refractive index and in melting point (Table I); (2) the diastereomeric *dl*-2,3-dibromopentanes have identical refractive indices but differ in boiling point, melting point and density (Table II); (3) there is little difference in the refractive indices of 1,2- and 2,3-dibromopentanes (Table II); (4) the isomeric 2-pentenes, with hydrogen bromide in glacial acetic acid, yield bromopentanes having somewhat different refractive indices (Table III).

From the properties of the pentenes and dibromopentanes, the following deductions can be drawn: (1) pentene samples boiling below 36.2° (760 mm.) contain some 1-pentene; (2) pentene prepared from 3-bromopentane is largely, if not entirely, *trans*-2-pentene; (3) pentene prepared from 2-bromopentane contains some 1-pentene; (4) the refractive index values of the dibromides cannot be used for the purpose of differentiating the normal pentenes, especially if the dibromides have been distilled at atmospheric pressure.

If 1-pentene is present in the pentene prepared from 2-bromopentane, the refractive index of the bromopentane resulting from hydrogen bromide addition would have a value below that given by *trans*-2-pentene, due to the fact that 1-pentene yields 2-bromopentane mainly, and this has a lower refractive index (2-bromopentane, 1.4412; 3-bromopentane, 1.4443).[11,12] If the assumption is made that pentene prepared from 2-bromopentane contains *cis*-2-pentene, also,

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(8) Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927).

(9) Van Risseghem, *Bull. soc. chim.*, **28**, 187 (1914).

(10) Wilkinson, *J. Chem. Soc.*, 3057 (1931).

(11) Lucas and Moyse, THIS JOURNAL, **47**, 1459 (1925).

(12) Clark and Hollonquist, *Trans. Roy. Soc. Can.*, [3] **24**, Sect. 3, 1115 (1930).

the comparatively low value of 1.4416 (3, Table III) is accounted for. It is possible that other samples of pentenes, including those obtained by irradiation,[3] might be mixtures of the three normal pentenes. If this is the case, then variations in the refractive index values of the bromopentanes may be due to different proportions of the three normal pentenes present in the hydrocarbon reacting. Since it is possible to account for the properties of the bromopentanes on this basis, and since there is no difference in the refractive index values of the two *dl*-2,3-dibromopentanes, the addition of hydrogen bromide to 2-pentene does not furnish experimental evidence for the hypothesis of electronic isomerism.

Experimental Part

α-Hydroxy-α-methylvaleric Acid, III.—In a 3-necked, 3-liter flask surrounded by a freezing-bath and provided with a mechanical stirrer, a thermometer and a dropping funnel, was placed 516 g. (6.0 moles) of 2-pentanone[7] and 330 g. (6.3 moles) of sodium cyanide (96–98%, powder). During vigorous stirring and over a period of forty to sixty minutes there was run in a cold mixture of 540 g. (6.0 moles) of C. P. concd. nitric acid and 500 g. of ice, keeping the temperature below 20° until near the end of the run, when it was allowed to rise to 25°. The water present in the reaction mixture was just sufficient to hold the sodium nitrate in solution. The crude cyanohydrin layer was separated and immediately mixed with 800 ml. (8 moles) of C. P. concd. hydrochloric acid in a flask provided with a reflux condenser. The mixture warmed spontaneously and the heat of reaction was sufficient to keep the flask contents boiling for about two hours. The refluxing was continued, by heating, for a total of eight hours. After cooling, 300 g. of water and 150 g. of anhydrous sodium sulfate were added, the mixture was well shaken, the oil phase was separated and the heavier mixture of aqueous and solid phases was extracted with ethyl ether. The combined oil and ether extracts were shaken with an aqueous solution of sodium sulfate and dried over the anhydrous salt. Fractionation gave some unchanged ketone (usually 100 to 125 g.), and 475 g. (60% yield on original ketone) of crude acid, b. p. 88–90° (1 mm.), m. p. 50–52°. Equivalent weight of crude acid: found, 133.4; theoretical, 132.1; after crystallization from toluene, m. p. 54–54.5° (corr.). The crude acid was used without purification.

Decomposition of the Hydroxy Acid.—This was best accomplished as follows: in a 500-ml. flask provided with a vertical neck holding a column of glass rings 15 cm. long by 2.5 cm. in diameter, 264 g. (2 moles) of III was heated at such a rate that in about twenty minutes the temperature of the liquid acid was about 210° and of the vapor about 160°. Up to this point water and some ketone distilled over. The receiver was changed and heating continued so that, in thirty to forty minutes, the liquid temperature rose to about 245° and the distilling temperature to about 220°. The residue was largely the lactide. The yield of crude IV was 80% and of lactide 20%. The crude acid contained considerable hydroxy acid and when redistilled at reduced pressure gave a 50% yield of IV from the original III. When the decomposition was carried out more slowly, the yield of redistilled IV rose to 71%. However, this procedure was less desirable since the resulting product contained less of the higher boiling *trans* isomer. The absence of α-propylacrylic acid was shown by ozonization[13] of some purified *trans* acid and of an intermediate fraction from subsequent distillation, which was a mixture of approximately equal parts of the *cis* and *trans* acids. Propionaldehyde in 60% yield was obtained in each case, but no formaldehyde. The residual lactide distilled at 82.5–84.3° under a pressure of 0.4 mm.; n^{25}_{D} 1.4475.

α-Methyl-β-ethylacrylic Acids (*cis* and *trans*).—The isomeric unsaturated acids were separated from each other by distillation under a pressure of 10 mm. through a column of glass rings, 50 × 3 cm. After three fractionations a fair separation was accomplished. From the higher boiling fractions, some of which solidified in an ice-bath, crystalline *trans* acid was obtained by crystallization from suitable solvents, *viz.*, ligroin (45–60°), toluene, *m*-xylene, carbon tetrachloride, ethyl ether, isopropyl ether, dibutyl ether, ethyl acetate, formamide, formic acid (85%). However, the purification was best accomplished by adding to 1 g. of the acid, 2 ml. of a 50% (by vol.) methanol–water mixture and allowing the solution to stand in a refrigerator at 3° for one to two days. From the lower boiling fractions a solid slowly crystallized when cooled by an alcohol-bath at −80°. At this temperature the liquid phase was very viscous and complete crystallization was accomplished only after two or three days. A separation of solid from uncrystallized liquid was not feasible because of the viscous nature of the latter. Dilution with solvents, for example ligroin (45–60°), chloroform, methanol, or ethanol, was no improvement, for no crystals separated, even at −80°. However, from methanol, on cooling to this temperature, a solid was obtained when water was added in the ratio of one mole per mole of acid. This, which was probably a monohydrate, was not investigated further. The approximate yield from the hydroxy acid was *cis* acid 30%, *trans* acid 20%. Data on the two acids are: b. p. at 10 mm., *cis*, 94.0–94.4°; *trans*, 106.5°; n^{25}_{D} *cis*, 1.4488; *trans*, 1.4578; m. p., *cis*, −42°, *trans*,[14] 24.1°; melting point of *p*-phenylphenacyl esters,[15] *cis*, 44.5–45.8°; *trans*, 90–91°.

When an attempt was made to prepare the dibromides of the two acids, by the action of bromine in carbon tetrachloride solution, the *trans* acid yielded a solid dibromide, m. p.[14] 97–8°, whereas the *cis* acid yielded an oil from which the same solid dibromide slowly separated.

Addition of Hydrogen Iodide.—The procedure previously described[5] was followed, except that the reactants were allowed to stand for a longer time (ten to thirteen days) in the dark at 2 to 3° and the temperature was kept at −15 to −20° during removal of the chloroform by pumping off. Also, residual chloroform was removed by continuing the pumping with a Hyvac pump for three hours

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[13] Following the procedure of Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).

[14] Von Lang, *Monatsh.*, **4**, 71 (1883), found a similar value.

[15] By the method of Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

at room temperature, all done in a dark room. The hydroiodide, V, when the *cis* acid was the starting material was a gum, and when the *trans* acid, a crystalline product which melted at 35.8–41.5°. On crystallization from ligroin (40–65°) it came out as long, glistening needles melting at 42.0–42.5°. The hydroiodides of the *cis* and *trans* acids were at once converted into the pentenes.

2-Pentene (*cis* and *trans*), **VI.**—The hydriodide from 38 g. (0.33 mole) of the unsaturated acid was dissolved quickly in a solution of 28.6 g. (0.26 mole) of sodium carbonate in 650 ml. of cold water (0°) and the solution was transferred quickly to a 3-necked 2-liter flask provided with a mechanical stirrer, thermometer and outlet tube. To the last was attached in order a spiral wash bottle of aqueous 18% sodium hydroxide surrounded by a water-bath at 45°, a short vertical condenser cooled by ice water, and below this a trap similarly cooled and connected to air by a reflux condenser cooled to −78°. The stirrer was started and immediately a gas was slowly evolved, the temperature having risen in the meantime to 7 or 8°. Heat was applied. The rate of evolution increased with rise in temperature. Finally, after about one and one-half hours the solution boiled and no more gas came over. In the case of the hydroiodide from the *trans* unsaturated acid the pentene was all generated by the time the reaction mixture had reached 40°, but in the case of the *cis* isomer this was not the case until 60° was reached. The yields of crude pentenes were: *cis*, 50–55%, from the *cis* unsaturated acid; *trans*, 85–90%, from the *trans* unsaturated acid.

The crude pentenes, after drying over calcium chloride, were slowly distilled through a spiral fractionating column of the Davis type,[16] made of 4.5 meters of 5 mm. i. d. Pyrex tubing in 25 coils, but with mechanical insulation instead of a vacuum jacket.[17] With a reflux ratio of 6:1, a good separation was accomplished from the main impurity of the pentene, which was chloroform. The residue from the first fractionation gave a faint isocyanide test. The chloroform was almost completely removed by one fractionation, for after a second distillation the refractive index of the main hydrocarbon fraction was practically identical with the previous value (within 0.0001 unit) and the index of the small residue was only 0.0004 higher than the main fraction in the case of the *cis* and 0.0002 higher in the case of the *trans* isomer. At the end of the first distillation these differences were 0.0086 and 0.0063, respectively. Judging by refractive index values, the percentages of chloroform in the residues of the first distillation were 13 for the *cis* and 10 for the *trans*, and in the residues of the second, 0.6 and 0.3, respectively. The physical constants of the two isomers are shown in Table I which gives in addition the values obtained by other investigators, and also the values for 1-pentene.

The properties of the *trans* isomer agree fairly well with the isomer synthesized by Lauer and Stodola (3, Table I). The pentene prepared by Norris and Reuter was a mixture of *cis* and *trans*-2-pentene. The products prepared by Sherrill and by Clark and Hollonquist from 3-bromopentane were probably fairly pure *trans*-2-pentene; those obtained from 2-bromopentane were mixtures of *cis* and *trans*-2-pentene with 1-pentene. The fact that they were mixtures with 1-pentene is indicated by the low boiling point and low refractive index. Naturally, the greater the contamination with 1-pentene, the greater the amount of 2-bromopentane formed when hydrogen bromide adds.

The Diastereomeric *dl*-2,3-Dibromopentanes.—These were prepared from the 2-pentenes with the usual precautions[5] and were distilled through a Weston column[18] while maintaining a reflux ratio of 40:1. Redistillation of the main fraction showed no change in the refractive index or boiling point. The values found are given in Table II, along with values of other investigators and the values for 1,2-dibromopentane.

It is desirable to point out several significant features in Table II. First, the refractive indices of the dibromides of *cis*- and *trans*-2-pentene are identical but the densities, boiling points and melting points are different. Second, the refractive indices agree well with the values observed by Norris and Reuter and by Van Risseghem, but not by Sherrill and co-workerrs. Third, the fact that the higher melting dibromide comes from the hydrocarbon which is the less pure, *i. e.*, the *cis*, would seem to indicate that the impurity is probably not significantly large. Fourth, the low refractive index reported by Sherrill indicates that at the temperature of distillation, 178–179°, their dibromides were either decomposing or undergoing isomeric change.[19]

Addition of Hydrogen Bromide to the Pentenes.—This was carried out in glacial acetic acid in the usual manner, and analysis was done by means of the refractive index,[2,3,11] rather than by conversion, through the Grignard reagent, to anilides.[4] This was done in order that the results would be comparable to those upon which Kharasch based his hypothesis of electronic isomerism. The data on the product from the *trans* isomer are reliable, for the bromopentane was obtained in 80% yield (from 4.7 g. of pentene) and the refractive index of the latter before distillation through a micro column with total reflux was identical with the index of the fraction after distillation. But the data on the *cis* product are not so dependable because the weight of product was much smaller, due to an accident. The data are shown in Table III.

Taken in conjunction with the conclusions drawn from the data of Table I regarding the compositions of the various pentenes prepared by others, the data in Table III account satisfactorily for their results when hydrogen bromide adds. Since the 2-pentene from 3-bromopentane was largely *trans*-2-pentene, one would expect the refractive index of the resulting bromopentane mixture to have the higher value (4, Table III); since the pentene from 2-bromopentane was probably a mixture of *cis*-2-pentene *trans*-2-pentene and 1-pentene, one would expect the bromopentane from this mixture to have the lower value (3, Table III). This last statement would be true, even if there were some error in the refractive index of the product from the *cis* isomer. Variations in the refractive index values of bromopentanes obtained from other pentene preparations[2,3,12] may be due, in part at least, to different

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[16] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

[17] This insulation was satisfactory since the boiling point of the pentenes is so close to room temperature.

[18] Weston, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

[19] Decomposition of dibromobutanes and dibromopentanes, when distilled at atmospheric pressure, has often been observed in this Laboratory. See also Young and Winstein, THIS JOURNAL, **58**, 102 (1936).

proportions of *cis*-2-pentene, *trans*-2-pentene and 1-pentene in the pentene.

Summary

1. The isomeric *cis*- and *trans*-2-pentenes have been synthesized from the pure *cis*- and *trans*-α-methyl-β-ethylacrylic acids. They have identical boiling points (35.4° at 740 mm.) but different refractive indices.

2. The diastereomeric *dl*-2,3-dibromopentanes obtained from the isomeric 2-pentenes by bromine addition have identical refractive indices but different boiling points, freezing points and densities.

3. Pentene prepared from 3-bromopentane appears to be the *trans* isomer, while that from 2-bromopentane is probably a mixture of *cis*-2-pentene, *trans*-2-pentene and 1-pentene. Pentene exposed to ultraviolet light is probably a mixture of these three hydrocarbons, also.

4. When hydrogen bromide in glacial acetic acid adds to the pure 2-pentenes, the resulting bromopentanes have different refractive indices.

5. The variation in the refractive index values of bromopentane mixtures obtained by other investigators when hydrogen bromide was added to different preparations of pentenes may be due to variable proportions of *cis*-2-pentene, *trans*-2-pentene and 1-pentene.

6. There is no experimental basis for the hypothesis of electronic isomerism of ethylene compounds.

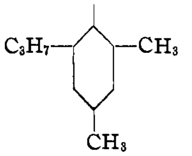
PASADENA, CALIF. RECEIVED JULY 6, 1937

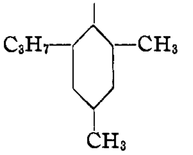
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Allyl 2,4,6-Trialkylphenyl Ethers

BY CHARLES D. HURD AND WILLIS A. YARNALL

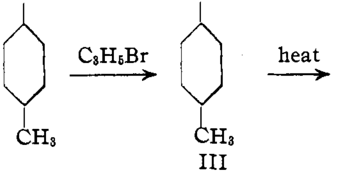
Claisen, who discovered that allyl aryl ethers undergo rearrangement at 200–250° into *o*- or *p*-allylphenols, subjected allyl 2,4-dimethyl-6-propylphenyl ether (II) to similar thermal treatment in order to see if the rearrangement could be forced to the meta position. He found[1] that it could not, but he did encounter thermal instability in spite of the inability to rearrange. The products were stated to be the phenol (I), allene, diallyl and resinous matter. The yield of allene was reported to be 10%, and of diallyl 50%. Claisen believed that the gas was allene because it yielded a white precipitate with mercuric chloride solution. He demonstrated the absence of the isomeric methylacetylene by observing a non-reaction toward ammoniacal silver nitrate or cuprous chloride.


I


II

This problem was reinvestigated because it seemed unlikely that the gas was allene. The "equation type of mechanism" favors allene, to be sure, since $ArOC_3H_5$ differs from ArOH by C_3H_4. However, the formation of the phenol without allene is comparable to the pyrolytic formation of methane without allene from butylene,[2] or of propylene without allene from diallyl,[3] or of aniline without allene from diallylaniline.[4] Propylene was formed in each reaction. The last of these reactions is particularly striking since diallylaniline, $C_6H_5N(C_3H_5)_2$, may be regarded as the ammono analog of phenyl allyl ether. It decomposes at about 250° with the evolution of propylene. Therefore, it seemed reasonable to believe that Claisen's gaseous product was propylene also.

Any of the allyl 2,4,6-trialkylphenyl ethers should behave like II in this decomposition. Accordingly, allyl 2,6-dipropyl-4-methylphenyl ether (IX) was selected because it was more accessible than II. It was prepared from 2-propyl-4-methylphenol (V) which in turn was synthesized from *p*-cresol by the following sequence of steps.


III

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[1] Claisen and Tietze, *Ann.*, **449**, 94 (1926).

[2] Hurd and Spence, THIS JOURNAL, **51**, 3566 (1929); Hurd and Goldsby, *ibid.*, **56**, 1812 (1934).

[3] Hurd and Bollman, *ibid.*, **55**, 700 (1933).

[4] Carnahan and Hurd, *ibid.*, **52**, 4586 (1930).