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THE PYROLYSIS OF MENTHOL

BY

JOHN JAMES WESTBROOK III

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
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FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

APPROVED:

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DEDICATION

To Ann and Laura

ACKNOWLEDGEMENT

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INTRODUCTION

Research on the pyrolysis of organic compounds has received an increasing amount of attention in recent years. The pyrolysis of terpene hydrocarbons has been of interest primarily because of their wide-spread and abundant natural occurrence. In addition terpenes have been investigated because of their interesting stereochemistry.

Menthol is a C_{10} monocyclic terpene alcohol. Its thermal decomposition at temperatures greater than 500°C has not been investigated previously because of inadequate methods of analysis.

The pyrolysis of other terpene hydrocarbons has revealed new routes to useful intermediates from relatively cheap source materials. Menthol, however, has never been considered as a possibility in these studies.

The stereochemistry of menthol has led to its extensive use in studying the mechanism of thermal elimination reactions.

The mechanism of thermal decomposition in pyrolysis reactions has been reported for several terpene hydrocarbons. Such investigations prior to this study, however, did not include menthol.

The objects of this investigation were; a) to study the pyrolysis of menthol from 450° to 750°C and determine the major products of the reaction both qualitatively and quantitatively, and b) to postulate and discuss mechanisms of the pyrolysis based on these results.

HISTORICAL

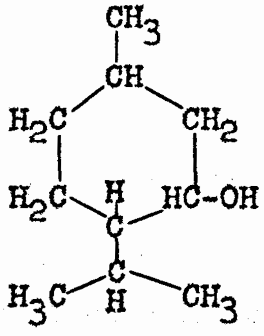
I. Menthol

A. Occurrence, Constitution, Physical Properties and Synthesis

Menthol, or "mint camphor", $C_{10}H_{20}O$, was first recognized as a crystalline principle in 1771 by the Dutch botanist Gambius, who termed it camphora europaea menthae piperitidis. Its main source, the peppermint plant, which finds mention in the Shin-J-Ho (984 A.D.) as Megusa, or eye herb, appears to have been cultivated in Japan for more than 2,000 years (90).

l-Menthol occurs in nature in the so-called peppermint oils, which are obtained from various species of Mentha piperita L. It is found mainly in the free state, the percentage of alcohol present in the oils showing considerable variation, dependent upon the habitat. Although natural menthol consists mainly of the crystalline l-menthol, it has been shown by Pickard and Littlebury (82) that the Japanese oil contains in addition a small percentage of the isomeric liquid d-neomenthol.

The constitution of menthol has been fully confirmed to be that shown in the following figure (101),



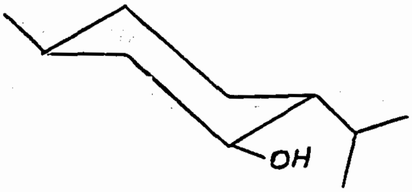
MENTHOL

Because of the distinctive anodynic, carminative, and antiseptic properties (72) of menthol, attempts have been made to investigate the individual physical properties (43, 82) as well as the pharmacodynamic activities (27) of its isomers.

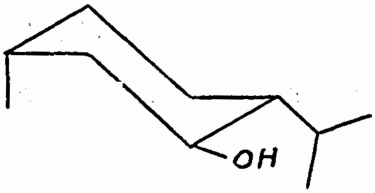
There are numerous syntheses of menthol. Those of commercial importance have been recently reviewed by Mignat and Porsch (73b).

B. Stereochemistry

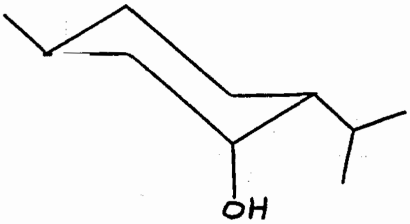
Menthol has three asymmetric carbon atoms. It can exist, therefore, in four externally compensated racemates and eight optically active forms or enantiomorphs (91, 101). The four stereoisomers of menthol are shown as follows,



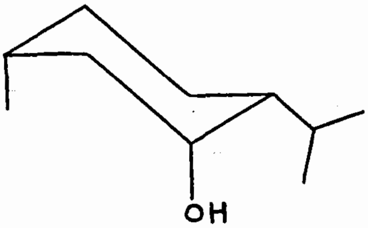
MENTHOL



ISOMENTHOL



NEOMENTHOL



NEOISOMENTHOL

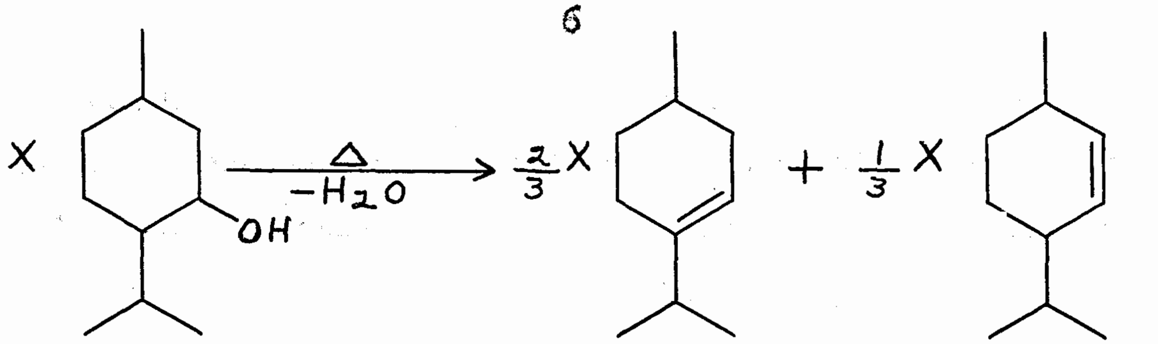
The four racemates and their eight optically active counterparts have been prepared. The first conformational proof of the four stereoisomers was reported by Read and Grubb in 1934 (91). Summaries of the stereochemistry of menthol have been published by Simonsen (101), Vila (116), and Mignat and Porsch (73a).

C. Analysis

Determining the composition of a mixture of isomeric menthols usually meant time-consuming and somewhat laborious separations based on physical properties and dissimilar reaction rates (44, 66, 92). Gas chromatography has recently afforded an excellent method or analysis of mixtures of stereoisomers (19, 63, 75, 89, 106).

II. Dehydration of Menthol and Related Terpene Alcohols

Menthol is best described as a monocyclic terpene alcohol. Its dehydration produces 3-p-menthene and 2-p-menthene by the following equation:



3-p-menthene 2-p-menthene

The first report of this reaction was made by Walter in 1836 (119) who showed that menthol when heated with phosphorous pentoxide produced a hydrocarbon. The constitution of menthol and menthene were not known at that time.

The dehydration of menthol to menthene was observed when menthol was heated with PCl_5 and $SOCl_2$ (125), Japanese acid earth (54, 78), active carbon (60, 61), reduced copper catalysts (40), phthalic anhydride (81), boric acid (77), dilute sulfuric and phosphoric acids (115), $ZnCl_2$ and $CuSO_4$ (17), and various organic acids (126, 127).

Inoue (54) studied the action of Japanese acid earth on menthol at 350°C and found that alkyl cyclopentanes were produced by skeletal rearrangement. Menthene, however, was the major product.

Recently Pines and Pillai (85) studied the dehydration of l-menthol and d-neomenthol over modified alumina catalysts. Evidence was obtained to show that trans elimination was the preferred mechanism with weakly acidic alumina catalysts.

von Rudloff (117) studied the dehydration of α-terpineol (1-p-menthene-8-ol) with acetic acid and acetic anhydride to produce menthadienes. For a comprehensive review of terpene alcohols and their dehydration to the corresponding olefins the reader is referred to Simonsen's "The Terpenes," Vol. I., The Cambridge Press, London (1947).

III. Pyrolysis of Menthol and Related Terpene Alcohols

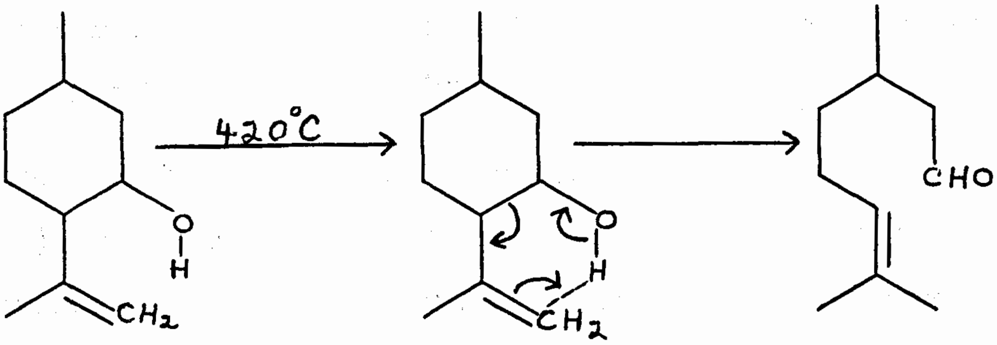
The pyrolysis of menthol has not been studied systematically at high temperatures in previous investigations due to inadequate analytical techniques.

Ipatieff (55) heated menthol in a bomb under pressure at 450°C and obtained menthene and a trace of menthone.

Treibs (110) reported the preparation of olefins by pyrolysis of the corresponding alcohols. This was done by passing the alcohol vapor through an electrically heated glass tube packed with unglazed potsherds. He also heated the alcohols in an autoclave and found that the temperature required to produce the olefins was reduced considerably. A temperature of 400°C was necessary to produce menthene from l-menthol with the heated tube. The autoclave reaction produced the same result at 250°C.

Ishikawa, et al. (56) passed melted menthol through a tube heated to 500°C. The main product was reported to be

3-p-menthene. They were interested in determining if any aldehydes were produced as in the pyrolysis of isopulegol (22, 33). Citronellal is formed through a cyclic mechanism by pyrolyzing isopulegol. The reaction is as follows,



ISOPULEGOL

CITRONELLAL

A similar reaction is reported for the pyrolysis of 1,8-p-menthadiene-3-ol (isopiperitenol) at 390-415°C to produce citral and isocitral (28).

Menthenes are not only obtained from the thermal decomposition of menthol but also from the thermal decomposition of its derivatives (21, 124). It is now noteworthy that numerous derivatives of menthol have been pyrolyzed in order to study the effects of stereochemistry on thermal elimination reactions. An excellent review has been written (21). The derivatives most frequently studied were esters. Their pyrolysis usually proceeds through a cis-elimination mechanism producing a mixture of 65% 3-p-menthene and 35% 2-p-menthene.

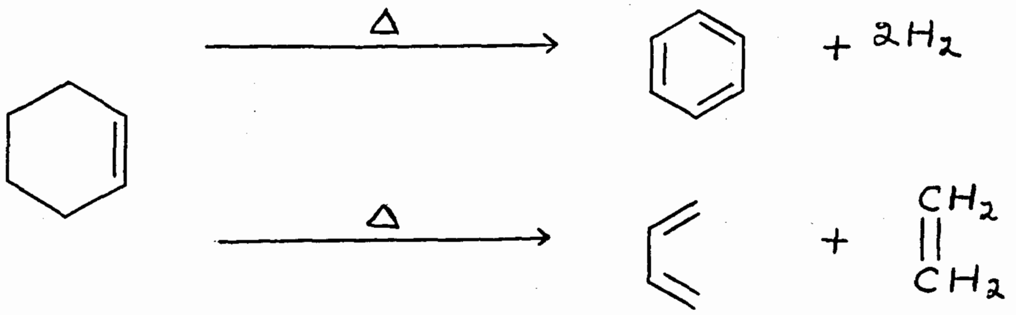
IV. Terpene Hydrocarbons

A. Pyrolysis

The para-menthenes are monocyclic terpene hydrocarbons. A large amount of information has been published on the pyrolysis of other terpene hydrocarbons. The thermal degradation of these compounds has been reviewed (23).

Rice and Murphy reported the pyrolysis of 3-p-menthene in 1944 (93) in a study of the thermal decomposition of substituted cyclohexenes. The reaction involved is commonly referred to as the reverse-diene or reverse Diels-Alder reaction.

If cyclohexene is heated above its decomposition point, at low pressures and for a time sufficiently short that only a small fraction is decomposed, it undergoes a simple dissociation into smaller molecules. The particular conditions mentioned were selected in order to avoid as far as possible bimolecular reactions of the products with each other or the substrate. Several thermodynamically possible decompositions might occur such as



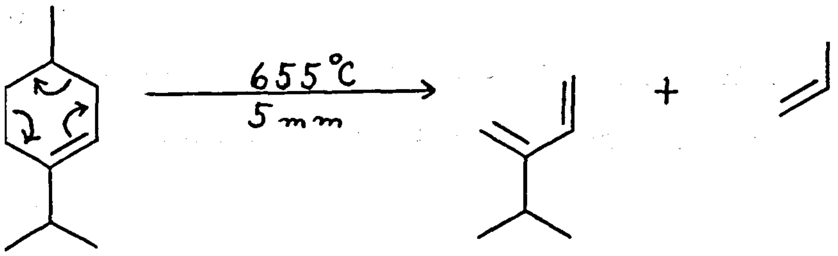
(I)

(II)

Reactions of these types were discussed in a previous publication by Rice and Teller (96) in the light of a principle called the principle of least motion. In the case of several reactions such as those listed above which are all thermodynamically possible, the principle states that reaction is favored which involves as little motion of the atoms as possible in passing from the old to the new configuration. The second half of the principle states that a reaction will be favored which involves least change of the electronic configuration of the reacting system. From both these standpoints, it is plausible to assume that the reaction will be favored which involves breaking or making as few bonds as possible.

On the basis of this principle they predicted that reaction II would be greatly favored over reaction I and this was found experimentally (95). No benzene was found in the products but butadiene and ethylene were formed in almost theoretical yield.

3-p-menthene was expected to decompose as follows,



No isopropyl butadiene was isolated in the pyrolyzate. Rice and Murphy assumed that the isopropyl butadiene was unstable under the conditions employed. They did observe, however, that 0.73 mole of propene was produced per mole of 3-p-menthene decomposed.

The pyrolysis of sabinene at 600°C yields β-terpinene and β-phellandrene (74).

Solanesol, a C_{50} polyunsaturated alcohol (97), has been shown to decompose at 500°C through a C_{10} biradical and an un-zipper mechanism (35). The primary product is dipentene.

The mechanisms of pyrolysis of α- and β- pinene (18), d-limonene (87), allo-ocimene (79), and 1,8-cineole (37) have also been described.

B. Thermal Isomerization and Disproportionation

The thermal isomerization of α- and β-pinene was reported by Goldblatt and Palkin (29).

Pines and Eschinazi (84) studied the isomerization of 1,2, and 3-p-menthene, respectively, in the presence of a sodium-organosodium catalyst. They observed that 2-p-menthene was readily isomerized to 1 and 3-p-menthenes. Neither of the products, however, isomerized to 2-p-menthene when subjected to the same reaction.

Eschinazi and Pines (24) also reported the disproportionation of d-limonene in the presence of a palladium hydroxide-barium sulfate catalyst. The p-menthenes isolated consisted mainly of 3-p-menthene. When 2-p-menthene was treated with this catalyst 3-p-menthene was the major menthene isolated in the products.

Hunter and Brogden (45) have recently shown that both isomerization and disproportionation of d-limonene occurs on silica gel. 3- and 2-p-menthene, respectively, were not isomerized by silica gel.

C. Analysis

The analysis of monocyclic terpene hydrocarbons has been greatly facilitated by the use of gas chromatography. The p-menthenes and p-menthadienes occur naturally in various essential oils. Close similarity of chemical structure, boiling point and other physical properties makes the separation of multicomponent mixtures of terpene hydrocarbons by conventional means extremely difficult.

Gas chromatography has been used successfully to separate these mixtures. Zubyk and Conner (128), von Rudloff (118), and Klouwen and ter Heide (64) have investigated the effect of various column parameters on the separation of monocyclic terpenes. Bernhard (14) studied the separation of terpenes using various polar liquid phases.

Ikeda, et al. (51) determined the monocyclic terpene hydrocarbon composition of twenty-nine non-citrus essential oils using a 1/4 in. X 10 ft. stainless-steel column packed with 25% (w/w) diethyleneglycol succinate (DEGS) on 60-80 mesh firebrick. This column should prove a valuable tool in analyzing the pyrolyzates of menthol at different temperatures.

V. High Temperature Pyrolysis

High temperature pyrolyses are those usually conducted within the temperature range 600°-900°C. The processes involved consist of preliminary breakdown of the starting materials into smaller fragments followed by extensive recombination, dealkylation, and dehydrogenation reactions which lead to aromatic products.

Weizmann (120) studied the aromatization obtained by cracking various hydrocarbon mixtures. Badger and co-workers (1-8) have made a study of the polynuclear hydrocarbons produced by pyrolyzing simpler hydrocarbons. Menthol, however, has never been the object of such investigations.

It is of interest to note that Hurd, et al. (47-50) recently published a series of papers on the pyrolytic formation of arenes. Hurd cited evidence from the literature and also demonstrated experimentally that contrary to the acetylene hypothesis of Berthelot (15) acetylene does not play an important role in the thermal decomposition and aromatization of most organic compounds.

Since menthol readily dehydrates to form 2-, and 3-p-menthene at relatively low temperatures, one might expect, therefore, thermal isomerization and disproportionation of the p-menthenes followed by extensive decomposition and recombination to produce aromatic products on pyrolysis of menthol from 450° to 750°C.

EXPERIMENTAL

I. Pyrolysis

A. Apparatus

The pyrolysis apparatus is shown in Figure I. It consists of a vertically mounted vycor tube (33 mm. O.D. X 300 mm.) fitted with a 7 mm. O.D. thermocouple-well. The tube is packed with 62.4 grams of porcelain saddles (6 mm.) and centered in a hinged-type combustion furnace. The furnace temperature is controlled by a Fisher pyrometer controller equipped with a 12 inch calibrated extension lead wire.

Two 250 ml. traps connected in series and cooled with a dry-ice acetone mixture are attached to the pyrolysis tube by vycor ground glass joints at appropriate positions. This arrangement furnishes an enclosed system which exits through the second trap into the atmosphere.

B. Procedure

The sample to be pyrolyzed is placed in a 150 ml. dropping funnel equipped with a pressure side arm and positioned at the

PYROLYSIS APPARATUS

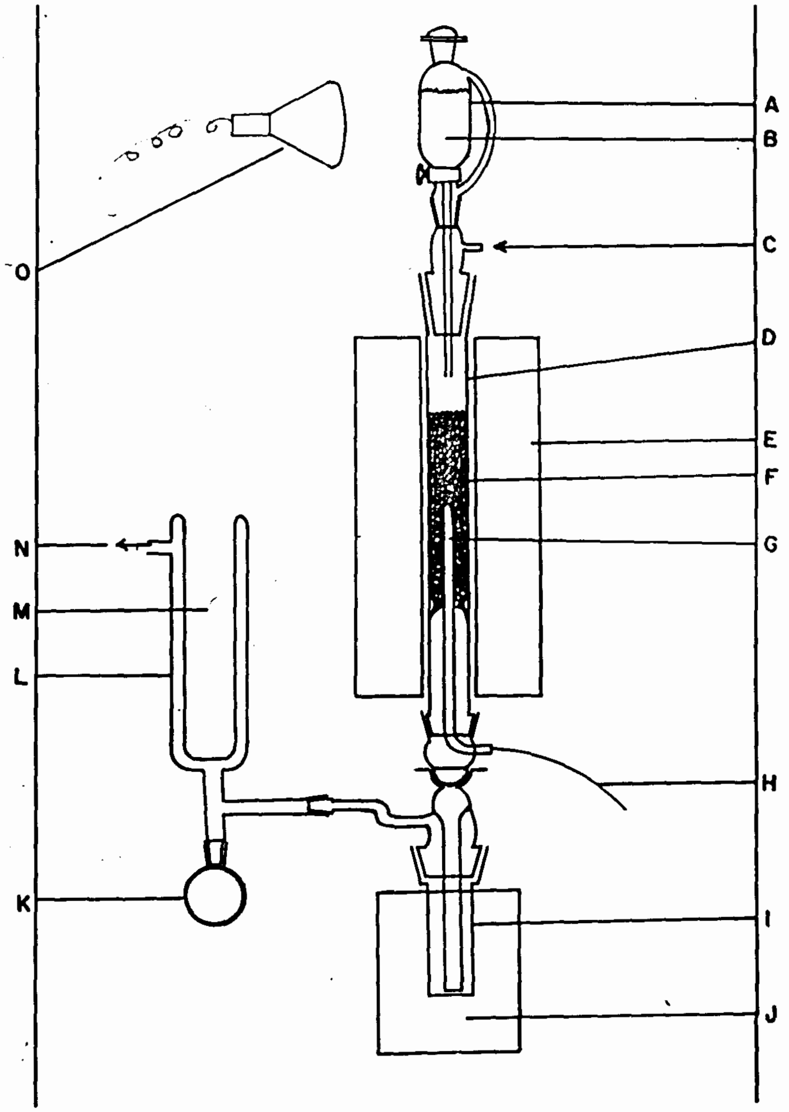


Figure I

Figure I

Key:

A. 150 ml dropping funnel
B. Sample
C. Helium inlet
D. Pyrolysis tube
E. Furnace
F. Porcelain saddles
G. Thermocouple-well
H. Thermocouple lead wire
I. 1st trap (250 mls)
J. Dry-ice acetone mixture
K. Collection flask (250 mls)
L. 2nd trap
M. Dry-ice acetone mixture
N. Exit port
O. Infrared heating lamp

top of the pyrolysis tube. A stream of dry Helium is introduced and the pyrometer controller set at the desired temperature for pyrolysis.

After the desired temperature is reached the traps are cooled with a dry-ice acetone mixture and the system allowed to equilibrate for 30 minutes. The Helium flow is then adjusted to 125 ml/min. with a soap-bubble flowmeter.

The sample is allowed to drop into the hot pyrolysis tube at a rate of approximately one gm/min.

Menthol is a solid at room temperature. It is kept in a melted state by heating to 50°C. with a small infrared lamp adjacent to the dropping funnel (see Figure I).

Upon completion of the pyrolysis the traps are disconnected and the pyrolyzate transferred to a suitable container and immediately weighed. The pyrolyzate is then stored at 0°C prior to analysis.

C. Compounds Pyrolyzed

1. Menthol:

1-Menthol (Yung-Zing Industries, Inc., Sao Paulo, Brazil, 99.6% pure by gas chromatography) was pyrolyzed at 450°, 550°, 650° and 750°C, respectively, in the manner described. The conditions of these pyrolyses are summarized in Table I.

Table I

Conditions of Pyrolysis

Compound	Temp. (°C.)	Grams Charged	Grams Collected	Time (min.)	Helium Flow (ml/min.)	Percent Recovery	Rate of Charge (gm/min.)	Contact Time (sec.)
Menthol	450	37.30	34.33	49.0	125	92.0	0.761	13.4
Menthol	550	36.30	31.30	35.0	125	86.2	1.037	13.4
Menthol	650	56.90	36.80	65.0	125	64.7	0.875	13.4
Menthol	750	44.80	23.254	45.0	125	51.9	0.996	13.4
2-isopropylbutadiene-1,3	750	10.10	4.10	12.0	125	40.6	0.842	13.4
3-p-menthene	750	8.30	2.60	9.0	125	31.3	0.922	13.4
α-methylstyrene	750	60.30	53.30	60.0	125	88.4	1.005	13.4
β-methylstyrene	750	32.70	24.00	30.5	125	73.4	1.072	13.4

The pyrolyzate at 750°C was fractionated prior to analysis using a conventional distillation apparatus with a receiving flask cooled in liquid nitrogen. The results of this separation are presented in Table II. The first fraction collected was immediately weighed and upon standing at room temperature three or four minutes began to boil at -30°C. A sample of the gas being evolved was trapped and analyzed mass-spectrometrically. The spectrum obtained showed the sample to be approximately 95% propene with a small amount of butadiene-1,3 and methane. The spectrum did not indicate the presence of acetylene.

2. 3-p-Menthene:

3-p-Menthene (Givaudan, Inc., 95% pure by gas chromatography) was pyrolyzed at 750°C. The conditions used are included in Table I.

3. 2-Isopropylbutadiene-1,3:

2-Isopropylbutadiene-1,3 was prepared by the method of Marvel, et al. (70), and distilled twice through a 14 X 1/2 inch glass column packed with glass helices. The fraction boiling at 86°-87°C was collected. The infrared spectrum matched the one previously published (71). The mass spectrum of this compound has never been reported. It is recorded in Table III.

The compound was pyrolyzed at 750°C. The conditions are given in Table I.

Table II

Distillation of Menthol Pyrolyzate at 750°C

Fraction	Boiling Point (°C.)	Weight of Fraction (gms.)	$d^{20°}$ (gm/ml)
*IA	-30° (760 mm)	3.00	---
IB	25° (760 mm)	2.20	0.73
II	20-40° (300μ)	13.984	0.860
H_2O	(present in II)	2.175	1.00
III	40-125° (200μ)	1.195	0.934
Residue	>125° (200μ)	0.700	---

*NOTE: Fractions IA and IB were collected as one fraction. The material which boiled off at -30°C. was found to be essentially pure propene.

Table III

Mass Spectrum of 2-Isopropylbutadiene-1,3

Mass to Charge Ratio (m/e)	Pattern Coefficient	Mass to Charge Ratio (m/e)	Pattern Coefficient	Mass to Charge Ratio (m/e)	Pattern Coefficient
25	0.32	51	12.57	80	3.88
26	5.31	52	6.84	81	100.00
27	48.02	53	37.68	82	6.50
28	4.09	54	15.10	83	1.34
28.5	0.06	55	14.73	84	0.32
29	6.21	56	4.58	85	0.11
30	0.22	57	0.42	88	0.09
31	0.10	59	0.11	89	0.13
34	0.11	60	0.09	91	0.77
35	0.13	61	0.46	93	0.60
36	0.13	62	1.02	94	0.38
37	1.66	63	2.11	95	3.77
38	4.16	64	0.50	96	28.80
39	37.93	65	5.88		
39.5	0.68	66	4.47		
40	5.70	67	12.80		
41	44.06	68	5.02		
42	4.05	69	3.17		
43	11.95	70	0.46		
44	0.67	73	0.15		
45	0.28	74	0.45		
46	0.32	75	0.65		
48	0.14	77	8.62		
49	0.91	78	4.21		
50	7.53	79	25.20		

4. α-Methylstyrene

α-Methylstyrene (Columbia Organic Chemicals, Inc.) was redistilled prior to use through a 14 X 1/2 inch column packed with glass helices in order to remove styrene. The fraction boiling at 162°C was collected and pyrolyzed at 750°C. The conditions are given in Table I.

5. β-Methylstyrene

β-Methylstyrene (Aldrich Chemical Co., Inc.) was redistilled prior to use through a 14 X 1/2 inch column packed with glass helices in order to remove the α-methylstyrene present as an impurity. The fraction boiling at 177°C was collected and pyrolyzed at 750°C. The conditions used are presented in Table I.

The densities of all the pyrolyzates were estimated to allow calculation of their volumes. These values were needed for determining the amounts of products isolated from the pyrolyzates. These data are presented in Table IV. Their use will be discussed later.

The pyrolyses at 650° and 750°C left carbon deposits on the pyrolysis tube and its packing. The tube and packing were, therefore, weighed before and after all of the pyrolyses were performed. The material left in the column never exceeded 40 ±10 mgs. The low recoveries at 650° and 750°C were due,

Table IV

Calculated Volume of Pyrolyzates (Corrected for Water)

Compound	Temp. (°C.)	Weight (gms)	$d^{20°}$	Volume (mls)
Menthol	750°			
*Fraction IB		2.20	0.73	3.0
Fraction II		13.984	0.860	16.26
Fraction III		1.195	0.934	1.28
Menthol	650°	33.292	0.849	39.21
Menthol	550°	30.755	0.858	35.84
Menthol	450°	34.10	0.877	38.88
2-Isopropylbutadiene-1,3	750°	4.10	0.840	4.88
3-p-menthene	750°	2.60	0.835	3.11
α-methylstyrene	750°	53.30	0.942	56.58
β-methylstyrene	750°	24.00	0.941	25.50

*note: The volume of Fraction IB was estimated by measuring an equal volume of water in the same flask. The density value reported was not measured directly.

therefore, to the inefficiency of the trapping system employed to trap the low-boiling compounds produced. Losses in transfer were greatest for the pyrolyzates at 450° and 550°C. The recovery data are presented in Table I.

The low recoveries, particularly those at 750°C, were investigated by analyzing the exit gases. A U-trap was connected to the exit port of the second trap (see Figure I) after the pyrolysis was begun. The trap was cooled with liquid nitrogen for five minutes and a sample of the gases collected and analyzed mass spectrometrically. The primary substance found was propene from the compounds pyrolyzed. Some ethylene was noted in the samples obtained from 2-isopropylbutadiene-1,3 and 3-p-menthene but in no case was acetylene observed.

The amount of propene in the exit gases from the menthol pyrolyses decreased sharply from 750° to 450°C. Only a trace was found from the pyrolysis at 450°C.

It is necessary to maintain a constant contact time and rate of charge in order to compare pyrolyzates at different temperatures.

Contact time is defined as the time the compound being pyrolyzed remains in contact with the pyrolysis tube packing. It is calculated by dividing the volume of packing by the flow rate of carrier gas in the system being used for pyrolysis.

Chromatogram Obtained from 10 μl of Fraction IB of the Menthol Pyrolysis at 750°C using a β,β'-Oxydipropionitrile Column

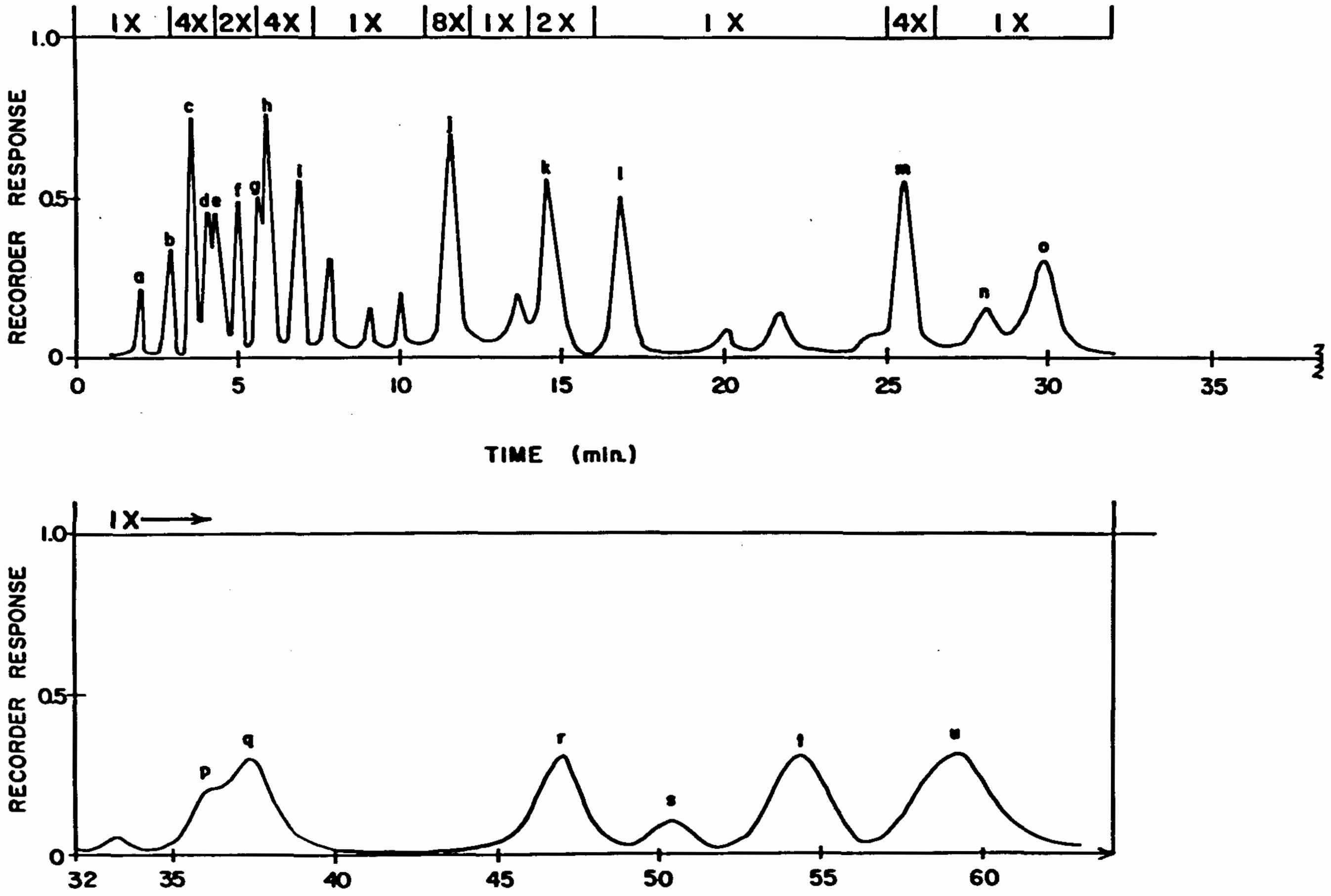


Figure II

Figure II

Key:	A.	Air
	B.	Propene
	C.	Isobutene
	D.	3-Methylbutene-1
	E.	Butene-2
	F.	Pentene-1
	G.	2-Methylbutene-1
	H.	Butadiene-1,3
	I.	2-Methylbutene-2
	J.	Isoprene
	K.	Pentadiene-1,4
	L.	Pentadiene-1,3
	M.	Cyclopentadiene-1,3
	N.	2-Isopropylbutadiene-1,3
	O.	2-Methylpentadiene-1,3
	P.	3-Methylpentadiene-1,3
	Q.	4-Methylcyclohexene
	R.	1-Methylcyclohexadiene-1,3
	S.	Acetaldehyde
	T.	Hexatriene-1,3,5
	U.	Cyclohexadiene-1,3

Chromatogram Obtained from 10 μl of Fraction II of the Menthol Pyrolysis at 750°C using a Diethyleneglycol Succinate Column

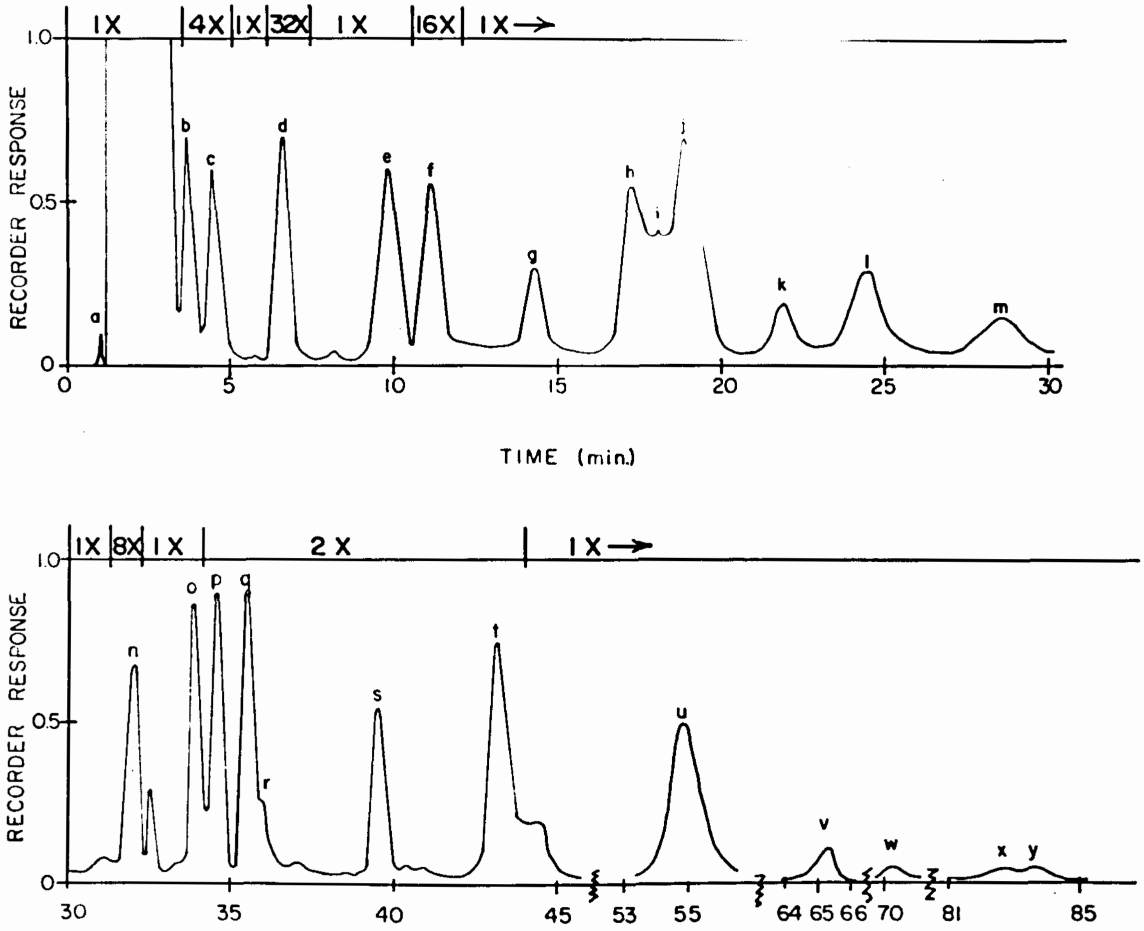


Figure III

Figure III

Key:
A. Air
B. 4-Methylcyclohexene-1
C. Cyclohexadiene-1,3
D. Benzene
E. 3-and 2-p-menthene
F. Toluene
G. 1-p-menthene
H. Ethylbenzene
I. p-Xylene
J. m-Xylene
K. Isopropylbenzene
L. o-Xylene
M. 4-Ethyltoluene
N. Styrene
O. α-Methylstyrene
P. p-Methylstyrene
Q. 3-Methylcyclohexanone
R. β-Methylstyrene
S. Indene
T. Menthol
U. Naphthalene
V. 2-Methylnaphthalene
W. 1-Methylnaphthalene
X. Phenol
Y. Biphenyl

acid esters for separating meta and para xylene in 1958. Pines and Pillai (86) reported the separation of 2-and 3-p-menthene using di-n-propyl tetrachloro-o-phthalate (7% on 30/60 mesh Chromosorb) at a column temperature of 120°C. The bis-(2-ethylhexyl)-ester used here was selected assuming that the branched alkyl group should further enhance the separation of 2-and 3-p-methene. The separation obtained, however, was essentially the same as that reported by Pines and Pillai. Table V lists the relative retention times of 1-, 2-, and 3-p-menthene for the n-propyl and 2-ethylhexyl esters. These values were calculated by dividing the observed retention time minus that of air by the retention time of toluene minus that of air.

The isomerization studies of menthenes mentioned previously (24, 45, 84) always yielded p-cymene as a product. p-Cymene was, therefore, an expected product from the pyrolysis of menthol and 3-p-menthene, respectively. It was observed that p-cymene and styrene are not separated on the DEGS column. These compounds were separated on a 15 foot by 1/4 inch column of Carbowax E-20M (20% by weight) on 60/80 mesh Chromosorb W. Column conditions were: block temperature, 250°C; injection port temperature, 215°C; column temperature, 125°C; helium flow, 50 mls per minute. Under these conditions styrene and p-cymene have retention times of 15.15 and 16.42 minutes, respectively. No peak for p-cymene was observed on the chromatograms from the pyrolyzates listed in Table VII.

Table V

Comparison of Tetrachlorophthalate Ester Columns

Compounds	Relative Retention Time di-n-propyl ester	 bis-(2-ethylhexyl) ester
Toluene	1.00	1.00
3-p-menthene	2.25	2.53
2-p-menthene	2.52	2.77
1-p-menthene	3.36	3.68

The limit of detection for most compounds using the F and M-500 GC-Unit is about 0.5 μg/μl. Compounds in mixtures such as reported here cannot be detected at this level and must be further concentrated to approximately 5.0 μg/ml to be detected and identified.

2. Identification of Products:

The exit port gases corresponding to chromatographic peaks were trapped in evacuated U-traps cooled in liquid nitrogen. The mass spectrum of each trapped compound was obtained using a Consolidated Electrodynamics Corp. Model 21-103C Mass Spectrometer.

Infrared spectra were determined by using a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer. The samples were collected for analysis by passing the exit port gases corresponding to a chromatographic peak through a 2 mm I.D. L-shaped glass tube inserted into a stoppered 3 inch test tube with a side arm. The test tube was cooled in liquid nitrogen during the collection.

Ultraviolet spectra were obtained using a Perkin-Elmer Model 350 Recording Spectrophotometer. Samples for this analysis were collected by passing the exit port gases through a 2 mm I.D. L-shaped glass tube inserted in a 5 ml vial filled with 3 mls of spectral grade cyclohexane. The elbow of the tube was cooled with a stream of dry air during the collection.

The identification of a chromatographic peak was considered positive only if the unknown spectrum was identical to the known mass, infrared or ultraviolet spectrum of the reference compound and if the retention time of the unknown peak was the same as that of the reference compound. All three spectra were obtained where possible.

The reference compounds were obtained from commercial sources. They were checked for purity by gas chromatography and used without further purification.

Due to slight variations (0.2-0.3 minutes) in retention times on duplicate chromatograms, the identity of retention times was additionally determined by adding 2 to 5 μg/μl of the reference compound to the pyrolyzate and observing that the height of the peak in question was increased without giving peak broadening or shoulders.

In Table VI are listed the compounds identified with their retention times on the columns described.

B. Determination

Known quantities of each compound identified were chromatographed. The resulting plots of peak height versus weight of sample were used to estimate the amount of each compound in the aliquot of pyrolyzate chromatographed. These weights were converted to percentage of the

Table VI

Identification of Compounds in Pyrolyzates

Compounds	Columns(a) Used For Identification	Retention Time (min.)	Methods(b) of Identification
propene	1	2.91	M.S., R.T.
isobutene	1	3.55	M.S., R.T.
3-methylbutene-1	1	4.05	M.S., R.T.
butene-2	1	4.30	M.S., R.T.
pentene-1	1	5.00	M.S., R.T.
2-methylbutene-1	1	5.65	M.S., R.T.
butadiene-1,3	1	5.85	M.S., R.T.
2-methylbutene-2	1	6.85	M.S., R.T.
isoprene	1	11.51	M.S., R.T.
pentadiene-1,4	1	14.35	M.S., R.T.
pentadiene-1,3	1	16.74	M.S., R.T.
cyclopentadiene-1,3	1	25.65	M.S., R.T.
2-isopropylbutadiene-1,3	1	28.10	M.S., R.T.
2-methylpentadiene-1,3	1	29.91	M.S., R.T.
3-methylpentadiene-1,3	1	36.00	M.S., R.T.
4-methylcyclohexene	1, 2	37.31, 3.77	M.S., R.T.
1-methylcyclohexadiene-1,3	1	47.00	M.S., R.T.
acetaldehyde	1	50.43	M.S., R.T.
hexatriene-1,3,5	1	54.32	M.S., R.T.
cyclohexadiene-1,3	1, 2	59.20, 4.49	M.S., U.V., R.T.
H_2O	----	----	I.R.
benzene	2	6.65	M.S., U.V., R.T.
3-p-menthene	2, 3	9.88, 15.03	M.S., R.T.
2-p-menthene	2, 3	9.88, 16.31	M.S., R.T.
toluene	2	11.13	M.S., U.V., R.T.
1-p-menthene	2, 3	14.25, 21.15	M.S., R.T.
α-phellandrene	2	17.65	M.S., U.V., R.T.
ethylbenzene	2	17.25	M.S., U.V., R.T.
p-xylene	2	18.10	M.S., U.V., R.T.
m-xylene	2	18.90	M.S., U.V., R.T.
isopropylbenzene	2	21.92	M.S., U.V., R.T.
o-xylene	2	24.40	M.S., U.V., R.T.
4-ethyltoluene	2	28.50	M.S., U.V., R.T.

Table VI

Identification of Compounds in Pyrolyzates (continued)

Compounds	Columns(a) Used For Identification	Retention Time (min.)	Methods(b) of Identification
styrene	2	32.12	M.S., U.V., I.R., R.T.
α-methylstyrene	2	33.96	M.S., U.V., R.T.
p-methylstyrene	2	34.65	M.S., U.V., R.T.
3-methylcyclohexanone	2	35.61	M.S., I.R., R.T.
β-methylstyrene	2	35.92	U.V., I.R., R.T.
indene	2	39.60	M.S., U.V., I.R., R.T.
menthol	2	43.10	M.S., I.R., R.T.
naphthalene	2	54.85	U.V., I.R., R.T.
2-methylnaphthalene	2	65.20	U.V., I.R., R.T.
1-methylnaphthalene	2	70.30	U.V., I.R., R.T.
phenol	2	82.80	U.V., I.R., R.T.
biphenyl	2	83.50	U.V., I.R., R.T.

(a) 1 = β,β′-oxydipropionitrile column
2 = diethyleneglycol succinate column
3 = bis-(2-ethylhexyl)-o,o′-tetrachlorophthalate column

See text for details.

(b) M.S. = mass spectral
U.V. = ultraviolet
I.R. = infrared
R.T. = retention time

pyrolyzate by substituting the observed values into the following equation:

$$\frac{(\text{micrograms found}) \text{ X } (\text{calculated volume of pyrolyzate in mls})}{(\text{aliquot volume in } \mu\text{l}) \text{ X } (\text{weight of pyrolyzate in mgs})} \text{ X } 100$$

= weight percent of compound in the pyrolyzate.

The results obtained are presented in Table VII for all of the compounds pyrolyzed.

The preliminary fractional distillation of the menthol pyrolyzate at 750°C did not allow the use of the above equation. In this case there was an overlapping of compounds in the fractions separated (Table II). The results in Table VII were calculated by determining the total amount of each compound in all of the fractions separated and dividing the respective sums by the total observed weight of the pyrolyzate.

There are, however, four compounds which could not be determined in the conventional manner just described. They are: propene, isobutene, butene-2, and butadiene-1,3. The low boiling points of these compounds makes it virtually impossible to inject known amounts at room temperature into a gas chromatography instrument.

Estimation of the amounts of these compounds present in the pyrolyzates was made as follows. A plot was made of millivolts response per microgram of compound chromatographed versus the corresponding retention time of all the compounds chromatographed

Table VII

Composition of Pyrolyzates by Weight Percent

Compounds	Menthol 750°C	Menthol 650°C	Menthol 550°C	Menthol 450°C	3-p-menthene 750°C	2-isopropyl-butadiene-1,3 750°C	α-methyl-styrene 750°C	β-methyl-styrene 750°C
propene	12.93	3.18	0.17	---	---	---	---	---
isobutene	1.33	2.74	0.19	---	---	---	---	---
3-methylbutene-1	0.37	0.53	0.07	---	---	---	---	---
butene-2	0.19	0.46	0.02	---	---	---	---	---
pentene-1	0.16	0.21	<0.01	---	---	---	---	---
2-methylbutene-1	0.67	0.85	0.04	---	---	---	---	---
butadiene-1,3	1.66	1.45	0.07	---	---	---	---	---
2-methylbutene-2	0.49	0.78	0.05	---	---	---	---	---
isoprene	2.32	2.11	0.08	---	0.77	1.88	---	---
pentadiene-1,4	0.63	0.53	0.03	---	---	---	---	---
pentadiene-1,3	0.38	0.27	0.01	---	---	---	---	---
cyclopentadiene-1,3	2.12	1.81	0.17	---	1.00	1.54	---	---
2-isopropylbutadiene-1,3	0.09	0.54	---	---	---	0.32	---	---
2-methylpentadiene-1,3	0.31	0.81	0.17	---	---	---	---	---
3-methylpentadiene-1,3	0.31	2.64	0.24	---	---	---	---	---
4-methylcyclohexene	0.72	6.14	0.42	---	2.81	2.29	---	---
1-methylcyclohexadiene-1,3	0.55	1.35	0.03	---	---	---	---	---
acetaldehyde	0.23	0.18	---	---	---	---	---	---
hexatriene-1,3,5	0.55	1.41	0.42	---	---	---	---	---
cyclohexadiene-1,3	0.57	1.73	0.77	---	1.08	0.32	---	---
H_2O	9.35	9.53	1.74	0.67	---	---	---	---
benzene	15.86	11.30	0.74	---	17.38	17.88	4.99	4.47
3-p-menthene	0.25	3.08	20.35	3.63	---	---	---	---
2-p-menthene	1.13	7.29	11.57	1.53	---	---	---	---

Table VII

Composition of Pyrolyzates by Weight Percent (continued)

Compounds	Menthol 750°C	Menthol 650°C	Menthol 550°C	Menthol 450°C	3-p-menthene 750°C	2-isopropyl-butadiene-1,3 750°C	α-methyl-styrene 750°C	β-methyl-styrene 750°C
toluene	10.65	10.58	0.70	---	21.62	18.12	3.46	4.50
1-p-menthene	1.16	---	5.79	0.86	0.05	---	---	---
α-phellandrene	---	---	0.72	---	---	---	---	---
ethylbenzene	0.95	1.39	---	---	2.58	1.17	---	---
p-xylene	0.76	1.44	---	---	2.08	1.54	---	---
m-xylene	1.27	1.99	---	---	3.85	2.78	---	---
isopropylbenzene	0.42	1.04	0.27	---	0.46	0.02	---	---
o-xylene	0.70	1.01	---	---	1.88	1.85	---	---
4-ethyltoluene	0.40	0.63	---	---	0.46	0.41	---	---
styrene	6.70	4.51	---	---	6.00	8.95	12.70	26.85
α-methylstyrene	0.43	0.57	---	---	1.15	0.54	52.99	1.37
p-methylstyrene	1.14	1.15	---	---	5.19	2.46	0.49	0.35
3-methylcyclohexanone	1.26	2.05	0.77	0.02	---	---	---	---
β-methylstyrene	0.37	0.22	---	---	0.62	0.20	0.87	12.24
indene	1.13	0.50	---	---	1.88	2.51	4.12	19.76
menthol	6.79	6.86	53.02	92.63	---	---	---	---
naphthalene	1.36	0.21	---	---	3.00	4.46	3.07	4.90
2-methylnaphthalene	0.45	0.17	---	---	1.42	2.73	0.88	0.44
1-methylnaphthalene	0.31	0.11	---	---	1.08	1.90	0.87	0.52
phenol	0.31	0.07	---	---	---	---	---	---
biphenyl	0.29	0.07	---	---	1.50	1.05	1.04	0.25
Total	90.02	97.47	98.62	99.34	77.86	74.92	85.48	75.65
Percent Undetermined	9.98	2.53	1.38	0.66	22.14	25.08	14.52	24.35

on the β,β'-oxydipropionitrile column. A level of approximately 50 micrograms was chosen for all compounds. A linear relationship which passed through the origin was observed for all compounds except 4-methylcyclohexene.

The millivolt per microgram response factor for the four compounds mentioned was estimated from the plot using their observed retention times. Substituting the observed response in millivolts from the pyrolyzate chromatogram into the following equation allowed an estimation of the amount present:

$$\frac{(\text{observed millivolts}) \times (\text{pyrolyzate volume in mls}) \times 100}{(\text{aliquot volume in } \mu\text{l}) \times (\text{response factor, mv}/\mu\text{g}) \times (\text{wt. of pyrolyzate in mgs})}$$

= weight percent of compound in pyrolyzate.

This method of calculation assumes that the response factors (mv/µg) of propene, isobutene, butene-2 and butadiene-1,3 obey the linear relationship observed for millivolts per microgram versus retention time. The values for these compounds in Table VII could be in error by ±30% of the amounts reported.

The values in Table VII are a reasonable approximation of the actual amounts in the pyrolyzates. Duplicate gas chromatograms were obtained from all of the pyrolyzates. A variation of ±5% of the millivolts response for each peak was observed. This is an excellent reproducibility.

The greatest source of error is encountered in the pyrolysis step. Two pyrolyses under identical conditions may vary by as much as ±20% relative. For example, a pyrolysis which yields 10 grams of pyrolyzate will give 8-12 grams on successive pyrolyses. The percentages of the constituents present in the pyrolyzates would, however, remain essentially the same.

The values in Table VII are at best minimum values. This is obvious from the recovery data in Table I. They can be used, however, to indicate the preferred pathways of decomposition and this is what was originally planned.

III. Discussion of Results

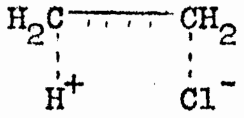
The pyrolysis of menthol between 450° and 750°C proceeds through a variety of reactions. These reactions vary from the relatively simple dehydration at 450°C to the complex formation of condensed aromatic compounds at 750°C as shown in Table VII. Free radical reactions appear to occur at 550°C and become more prominent at 650° and 750°C. The major reactions at 650° and 750°C lead to extensive aromatization.

The pyrolyses of several aliphatic compounds at lower temperatures do not seem to involve free radicals, since there is no inhibition by substances such as nitric oxide, propene, cyclohexene or toluene, which react with free radicals to give less active products (13, 99, 104) but appear to be concerted unimolecular decompositions. Some examples are shown in Table VIII.

Table VIII

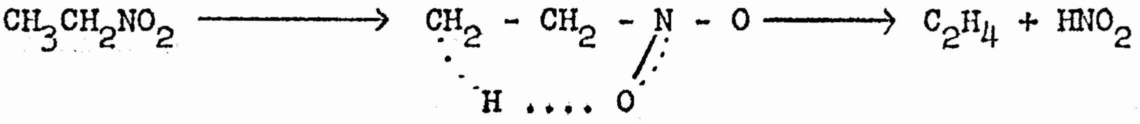
Reaction	A sec^{-1}	E kcal/mole	Reference
cyclobutane ⟶ $2C_2H_4$	$7.8X10^{15}$	62.5	25
cyclopentane ⟶ H_2 + cyclopentadiene	$1.1X10^{13}$	58.8	114
t-butanol ⟶ isobutene + H_2O	$3.2X10^{11}$	54.5	9a
n-propyl chloride ⟶ C_3H_6 + HCl	$2.8X10^{13}$	55.0	11a
sec-butyl bromide ⟶ HBr + butene-2	$4.3X10^{12}$	43.8	68
cyclohexyl bromide ⟶ HBr + cyclohexene	$3.2X10^{13}$	46.1	31
methyl chloride ⟶ HCl + 2-and 3-p-menthene	$1X10^{13}$	45.0	11b

In general the concerted unimolecular elimination of hydrogen halide, uncomplicated by other processes, only occurs with normal alkyl chlorides and alkyl bromides containing a secondary or tertiary C-Br bond (32). It has been suggested (53a) that the halide decompositions proceed via an ionic transition state, e.g.



$$\begin{array}{ccc} H_2C & \cdots\cdots & CH_2 \\ \vdots & & \vdots \\ H^+ & & Cl^- \end{array}$$

An extensive study (123) of the pyrolysis of nitroethane in flow and static systems showed that, though the reaction is first-order, the pre-exponential factor and the activation energy increase as the temperature is raised. Between 320° and 440°C, $k = 6.3 \times 10^{10} \exp(-39{,}700/RT)\ \mathrm{sec}^{-1}$, and the entropy of activation is about -11 cal. degree^{-1} mole^{-1}, suggesting that ethylene splits off unimolecularly, the transition state having a ring structure, i.e.



$$CH_3CH_2NO_2 \longrightarrow CH_2 - CH_2 - N - O \longrightarrow C_2H_4 + HNO_2$$

Above 490°C, the velocity constant of the decomposition in a very fast flow system is given by the expression $k = 4.0 \times 10^{17} \exp(-60{,}600/RT)\ \mathrm{sec}^{-1}$. The overall activation energy has risen to about the value of the dissociation energy of the $C_2H_5 - NO_2$ bond, indicating that the primary process is now fission of this bond.

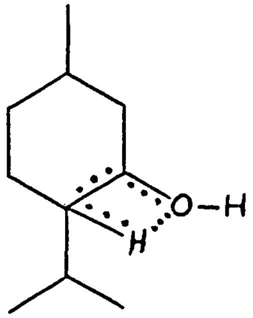
This is supported by the earlier results of Gray, Yoffe and Roselaar (30) who also investigated and discussed the pyrolysis of other nitroalkanes. With other hydrocarbons, e.g. cyclic hydrocarbons which undergo concerted unimolecular decomposition at lower temperatures, a free radical mechanism will occur when the temperature becomes high enough, since fission of a relatively weak C-C bond will then become appreciable.

The more pronounced types of reactions which probably occur during the pyrolysis of menthol from 450° to 750°C will now be presented.

A. Dehydration

The results obtained in this work from the pyrolysis of menthol at 450° and 550°C are in accord with those published previously (56, 110).

Dehydration which results from the concerted unimolecular elimination of water can be described as a "four-center" reaction (16). The reaction is assumed to proceed through a transition state represented as follows:



The reactions in Table VIII discussed previously are examples of this type of elimination.

The data from the pyrolyses of menthol at 650° and 750°C (Table VII) show that 3-,2-, and 1-p-menthenes are formed at these temperatures. This dehydration-isomerization reaction requires a relatively low energy of activation.

The reaction of nitroethane discussed previously went through a transition to a high activation energy type reaction. One would expect that menthol would behave similarly but the data (Table VII) show that the menthenes are still produced at 650° and 750°C.

It is proposed, therefore, that the dehydration of menthol at these temperatures is one of the initial reactions and is occurring simultaneously with reactions which usually require a higher activation energy, e.g. the thermal fission of C-C and C-H bonds.

B. The Reverse Diene Reaction

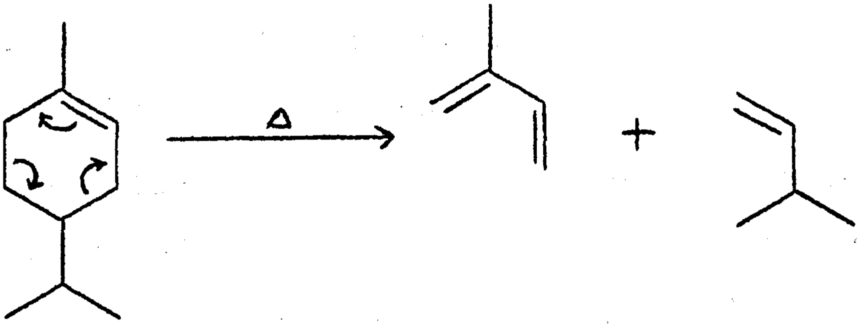
The reverse diene or reverse Diels-Alder reaction is well established (39, 80, 93, 122). It was cited earlier in a discussion of the work of Rice and Murphy (93) who observed that substituted cyclohexenes did not decompose as expected unless the substituted group was methyl, vinyl, or phenyl. 1-Ethylcyclohexene and 3-p-menthene did not produce the expected 2-ethyl and 2-isopropyl butadienes, respectively. These pyrolyses were conducted at 650° to 750°C. Rice and Murphy assumed that the ethyl and isopropyl butadienes suffered extensive secondary types of decomposition and were, therefore, not detected in their analysis of the pyrolysis products. They further concluded that the reverse diene reaction was probably not operative in the pyrolysis of 3-p-menthene. These pyrolyses were conducted at 650° to 750°C and it is noteworthy that isoprene was found to be quite stable at these temperatures. The results obtained in the author's study support this observation. The inadequacy of Rice and Murphy's method of analysis should also be considered.

In order to determine whether or not the reverse diene reaction was occurring during the pyrolysis of menthol, 3-p-menthene was pyrolyzed at 750°C (Table VII). A gas chromatogram of the pyrolyzate indicated that 2-isopropylbutadiene-1,3 might be present but the amount was too small to identify and determine. One might conclude, therefore, that 2-isopropylbutadiene-1,3 is either not formed or is thermally unstable at 750°C and thus undergoes decomposition immediately upon being formed.

A resolution of this question was sought by pyrolyzing 2-isopropylbutadiene-1,3 at 750°C. Only 0.13% of the amount charged was recovered in the pyrolyzate. This is an excellent indication of the thermal instability of the compound.

The pyrolyzates of menthol at 650° and 750°C (Table VII) did contain 2-isopropylbutadiene-1,3, which indicates that the reverse diene reaction of 3-p-menthene is probably occurring.

The isoprene formed in the pyrolyses of menthol and 3-p-menthene can be produced from 1-p-menthene by the reverse diene reaction as follows;



The 1-p-menthene is most likely formed by the isomerization of 2-p-menthene. Since 1-p-menthene and isoprene are formed during the pyrolysis of both menthol and 3-p-menthene (Table VII), we may assume that at least part of the isoprene is formed by the reverse diene reaction.

The pyrolyzates of 3-p-menthene and 2-isopropylbutadiene-1,3 at 750°C have a product composition very similar to the menthol pyrolyzate at 750°C. It is proposed, therefore, that the decomposition route - menthol ⟶ 3-p-menthene ⟶ 2-isopropylbutadiene-1,3 ⟶ products is a major one in the pyrolysis of menthol. The reverse diene reaction is thus a key reaction in the decomposition of menthol.

C. Free Radical Reactions

1. Homolysis:

The production of free radicals during pyrolysis reactions was demonstrated by Rice and Rice (94).

The strengths of chemical bonds are expressed as the bond dissociation energies in kcal. per mole (20, 111). Generally C-C bonds have lower dissociation energies than C-H bonds by 10-15 kcal. per mole. Two exceptions are the C-H bonds in the methyl groups of toluene and propene.

It was established in work with biallyl, 4-methylpentene-1, allylcyclohexane and 4-phenylbutene-1 that an allylic C-C bond is relatively weak toward pyrolytic scission (46). Pyrolysis of terpene hydrocarbons (83, 85, 87) displays the same weakness toward thermal rupture at allylic positions.

2. General Reactions of Free Radicals:

The free radicals generated by bond homolysis can undergo the following general types of reactions (111):

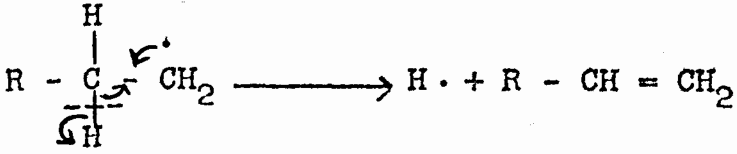
(a) Recombination, which is the reverse of bond homolysis

$$R\cdot + R\cdot^{*} \longrightarrow R - R^{*}$$

(b) Abstraction of hydrogen

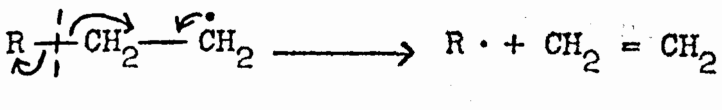
$$R\cdot + H - R^{*} \longrightarrow RH + R\cdot^{*}$$

(c) Loss of hydrogen



$$R - \underset{H}{\overset{H}{C}} - \dot{C}H_2 \longrightarrow H\cdot + R - CH = CH_2$$

(d) Loss of an alkyl fragment



$$R - CH_2 - \dot{C}H_2 \longrightarrow R\cdot + CH_2 = CH_2$$

which is the reverse of the addition of a free radical to an olefin, and

(e) Disproportionation

$$2CH_3 - CH_2\cdot \longrightarrow CH_2 = CH_2 + CH_3 - CH_3$$

Comparison of (c) and (d) shows that the loss of hydrogen radical with formation of an olefin has an activation energy of 35-45 kcal. per mole, while loss of an alkyl radical [R·, reaction (d)] has an activation energy of 25-30 kcal. per mole (16). Consequently, reaction (d) plays a larger role, and fragmentation of alkyl radicals to give lower molecular weight products predominates over dehydrogenation until quite high temperatures are reached. The occurrence of this reaction can be illustrated in the mechanisms postulated for the pyrolysis of menthol as shown in Figure IV. The products actually isolated in the menthol pyrolyzates are numbered.

Other instances of the dealkylation reaction (d) will be noted throughout subsequent discussion.

Reaction pathway (A) in Figure IV is based on the observations of Barnard and Hughes (9b, 10) who studied the pyrolysis of normal aliphatic alcohols. They found that the decomposition of n-butanol between 570° and 630°C is first-order, with an overall activation energy of 57 kcal. per mole, and gives hydrogen, carbon monoxide, methane, formaldehyde and smaller amounts of ethane, ethylene, propane and propene. The mechanism they suggested has the following

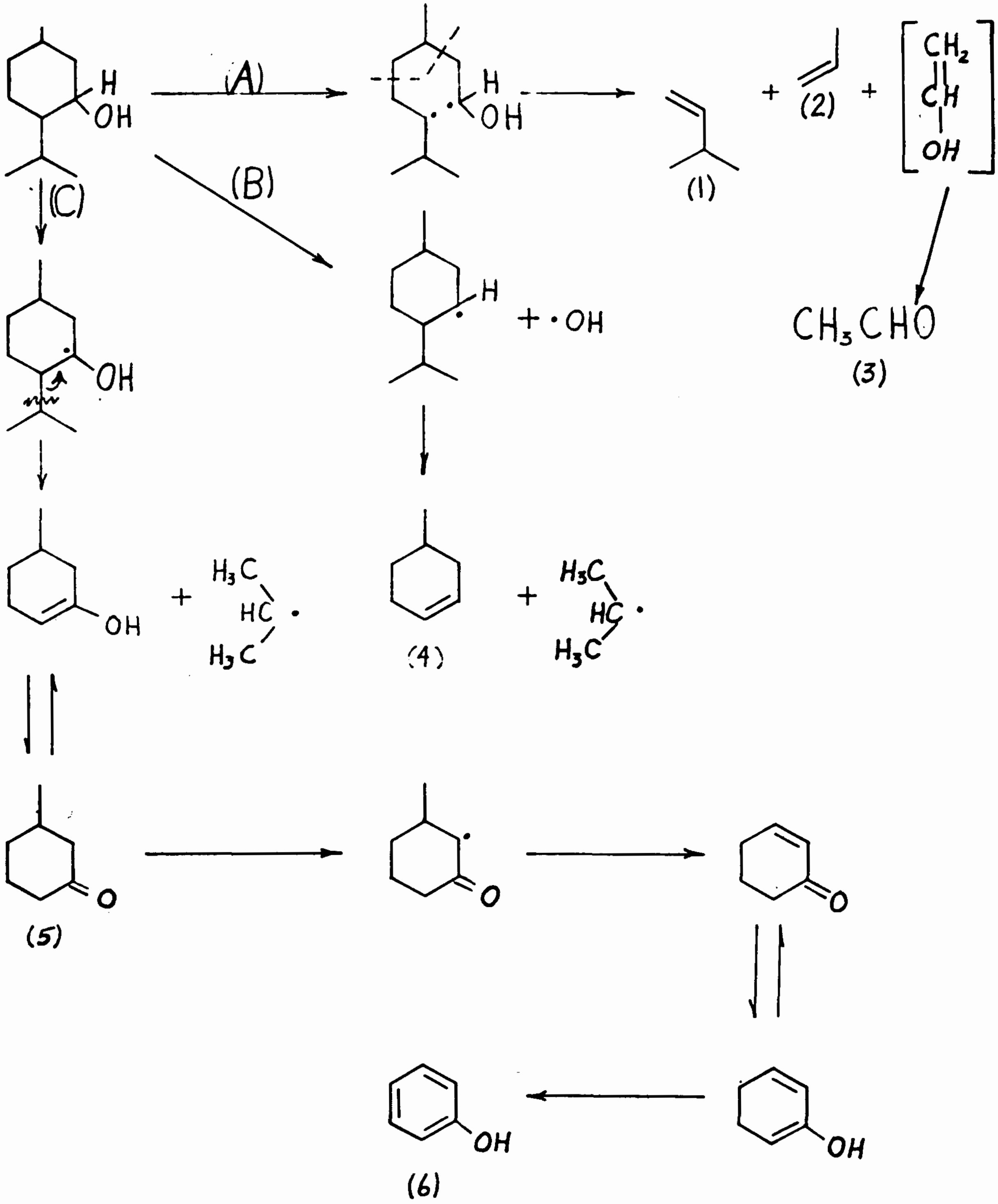
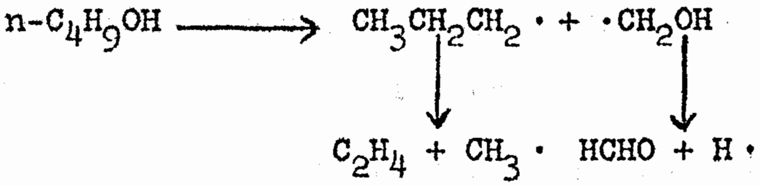


Figure IV

initial reaction:



$$n\text{-}C_4H_9OH \longrightarrow CH_3CH_2CH_2\cdot + \cdot CH_2OH$$

$$CH_3CH_2CH_2\cdot \longrightarrow C_2H_4 + CH_3\cdot \qquad \cdot CH_2OH \longrightarrow HCHO + H\cdot$$

which demonstrates that the primary rupture of bonds in aliphatic alcohols at elevated temperatures occurs at the carbon atom to which the OH group is attached. Reaction pathway (A) is merely an extension of this mechanism to cyclic alcohols.

The results in Table VII show that 3-methylcyclohexanone and 4-methylcyclohexene are formed during the pyrolysis of menthol at 550° and 650°C. It is probable, therefore, that these compounds are formed at these temperatures by reactions (B) and (C), respectively, as illustrated in Figure IV.

The homolysis of allylic bonds discussed previously is also occurring in the pyrolysis of menthol but discussion will be reserved for the moment.

D. Methyl Group Rearrangement

The migration or isomerization of methyl groups in free radical reactions has been demonstrated by Kharasch, et al. (59) who studied the reactions of di-t-butyl carbinyl radical. Trotman-Dickenson has discussed these reactions (111).

Tsutsumi and Nakamura (112) studied the thermal isomerization of O-, m-, and p-xylene from 550° to 700°C at 130 mm pressure. Their results indicate that the thermal stability of the xylenes decreases in the order; meta > ortho > para. It is of interest to note that ethylbenzene was one of the products obtained.

A comparison of the results obtained by Tsutsumi and Nakamura with those presented in Table VII is given in Table IX. There is a striking similarity between the results they obtained from p-xylene and those obtained from menthol, 3-p-menthene, and 2-isopropylbutadiene-1,3. This does not imply that the xylenes are formed during the pyrolysis of menthol via p-xylene. It is probable, however, that some isomerization of the xylenes might occur at 650° and 750°C under the pyrolysis conditions used by the author.

β-Methylstyrene (propenylbenzene) and indene were observed in the pyrolyzates of 3-p-menthene and 2-isopropylbutadiene-1,3 at 750°C and menthol at 650° and 750°C. The mechanism by which these compounds form was not clear from the information cited in the literature.

Herrington and Rideal (38) demonstrated that β-methylstyrene and indene were formed in the aromatization of propylene over various metallic oxide catalysts. Such a reaction from menthol, however, would involve extensive decomposition, recombination or resynthesis, followed by dehydrogenation and isomerization.

Weizmann, et al. (120) stated that allylbenzene produced

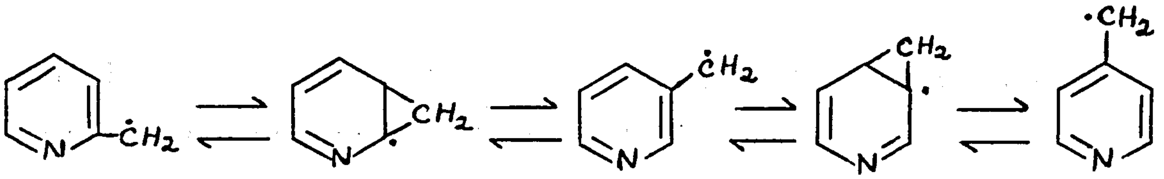
Table IX

Relative Amounts of Xylenes

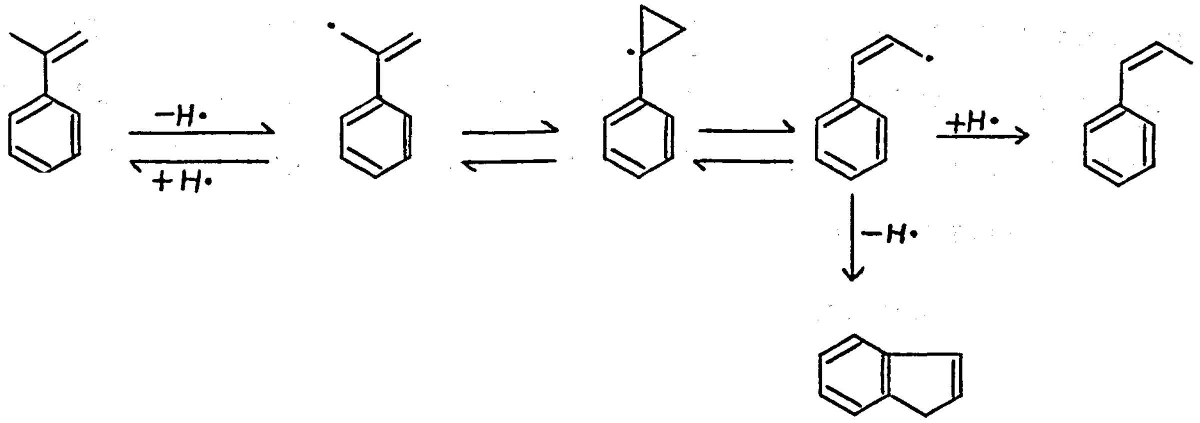
Compound Pyrolyzed	Temp. (°C.)	% ortho	% meta	% para	Ref.
o-xylene	650°	53	32	15	(112)
m-xylene	650°	0	80	20	(112)
p-xylene	600°	22	50	28	(112)
menthol	750°	25	47	28	Table VII
menthol	650°	23	45	32	Table VII
3-p-menthene	750°	24	49	27	Table VII
2-isopropyl-butadiene-1,3	750°	30	45	25	Table VII

chrysene in good yield when pyrolyzed at 650°C. The reaction is also accompanied by isomerization of allylbenzene to β-methylstyrene, and by degradation to toluene. These authors postulated that indene was formed from C_6-C_3 compounds such as β-methylstyrene but did not elaborate further on the mechanism involved.

More recently, Hurd, et al. (47-50) pyrolyzed 2-methylthiophene and obtained 3-methylthiophene as a product. The pyrolysis of 2-, 3-, and 4-methylpicoline, respectively, produced mixtures containing the other two isomers. To explain this, they postulated a "wandering methyl radical" by way of an intramolecular cyclic transition state as follows;



α-Methylstyrene was thus believed to be the precursor of β-methylstyrene and indene in the pyrolysis of menthol as indicated in the following scheme;



In order to determine the plausibility of such an isomerization, α-, and β-methylstyrene were pyrolyzed at 750°C, respectively.

A previous pyrolysis of α-methylstyrene illustrated that this compound is quite stable at 550°C (69). The pyrolysis of β-methylstyrene has not been previously reported in the literature.

The results in Table VII indicate that the proposed isomerization of α- to β-methylstyrene occurs and is reversible.

The rather large production of styrene from the pyrolyses of α-and β-methylstyrene illustrates that groups substituted in a vinyl position are rather easily cleaved at 750°C.

One of the primary products from the pyrolysis of β-methylstyrene is indene. The pyrolysis of indene to produce chrysene is a well known reaction (4d, 102, 120).

Although the proposed mechanism is not the only one which might be used to explain the formation of β-methylstyrene and indene, it is probably the major pathway to these products from the pyrolysis of menthol.

The pyrolysis of 2-isopropylbutadiene-1,3 at 750°C yielded essentially the same product mixture as 3-p-menthene and menthol (Table VII) except for the low molecular weight compounds which were either not collected or reacted to form other products.

It is probable that the "wondering methyl radical" isomerization is a principal decomposition pathway of 2-isopropylbutadiene-1,3 which leads to the formation of low molecular weight mono and di olefins as shown in Figure V. The compounds numbered were isolated in the pyrolyzates of menthol from 550° to 750°C.

E. The Diene Reaction and Dehydrogenation

The cyclization of paraffinic hydrocarbons into aromatics was originally described (42, 88, 105, 109, 113) as a three-step process: dehydrogenation of the paraffin hydrocarbon to a corresponding olefin, cycloisomerization of this olefin to a hexahydrobenzene, and simultaneous removal of the supernumerary hydrogen atoms from the latter to form the aromatic hydrocarbon. This process is catalyzed by various oxides which are used either in the pure state or supported on carriers such as alumina.

This reaction mechanism, however, could not account for the formation of aromatics by thermal cracking in empty or packed tubes (34, 100) without the presence of a catalyst. Two alternative mechanisms were proposed.

Both suggest that in the first stage of the reaction the starting material undergoes considerable breakdown, followed by resynthesis. Groll (34) assumed that the key intermediate was acetylene or, rather, a diradical form of that hydrocarbon, whereas other workers (36, 98, 120, 121) believed this intermediate was butadiene. The latter is known to combine with other unsaturated hydrocarbons, e.g. with ethylene to form cyclohexene (58), or with

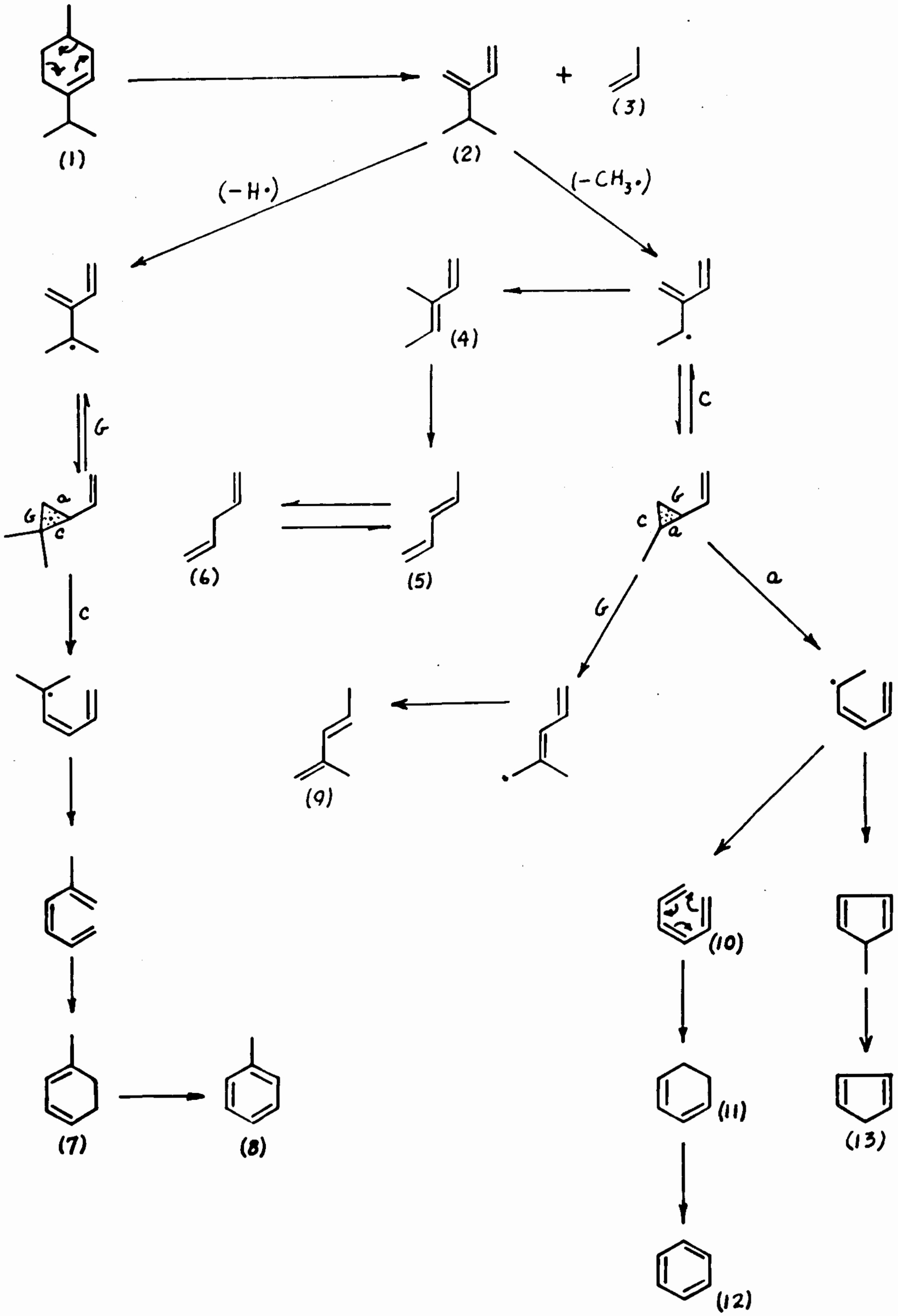


Figure V

a second molecule to form 4-vinylcyclohexene (12). This reaction is an extension of the classical Diels-Alder synthesis (41) and was first hypothesized by Hague and Wheeler (36) and by Schneider and Frolich (98). The reaction is still referred to as the Hague-Wheeler mechanism. This mechanism has also been used to explain the formation of alkyl cyclohexenes, cyclohexadienes and aromatics produced in the pyrolysis of terpene hydrocarbons (83, 85, 87).

Tarasenkova (108) has studied the formation of xylenes from the pyrolysis of butadiene with various butenes at 500° to 600°C.

Examples of the diene reaction which probably occur in the pyrolysis of menthol are presented in Figure VI. Those compounds actually isolated from the menthol pyrolyzates are numbered.

The last step in the formation of aromatic compounds by the diene reaction is dehydrogenation. It should be noted that the hydrogen atoms involved are allylic and for this reason are easily removed.

Direct dehydrogenation of menthol can also occur to produce aromatic compounds. This reaction also involves cleavage of allylic C-C and C-H bonds but does not require the diene reactions shown in Figure VI. The mechanism for the reaction is presented in Figure VII (those compounds isolated in the menthol pyrolyzates are numbered). Isopropylbenzene probably forms by this mechanism during the pyrolysis

The Diene Reaction in Menthol Pyrolysis

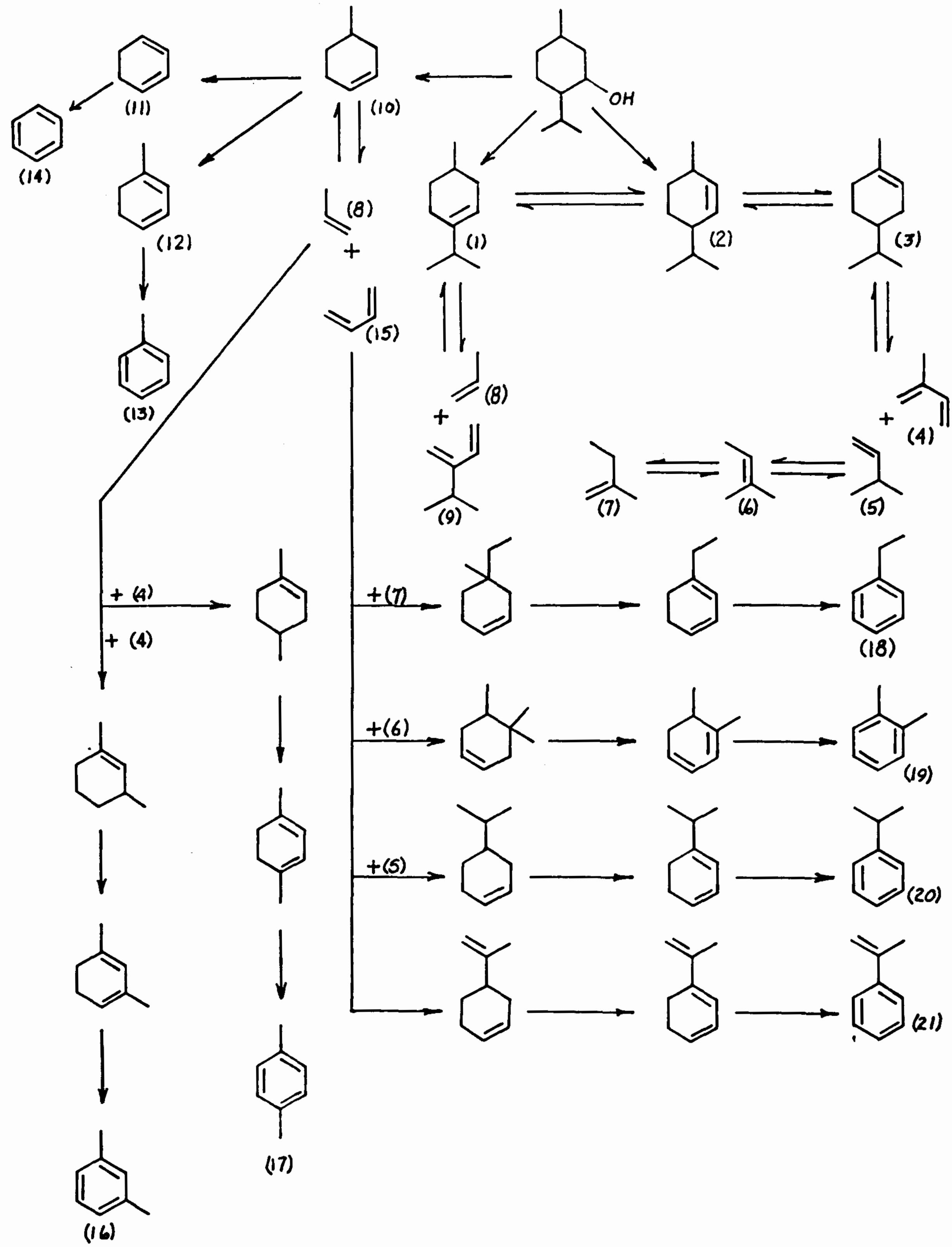


Figure VI

Direct Dehydrogenation and Dealkylation in Menthol Pyrolysis

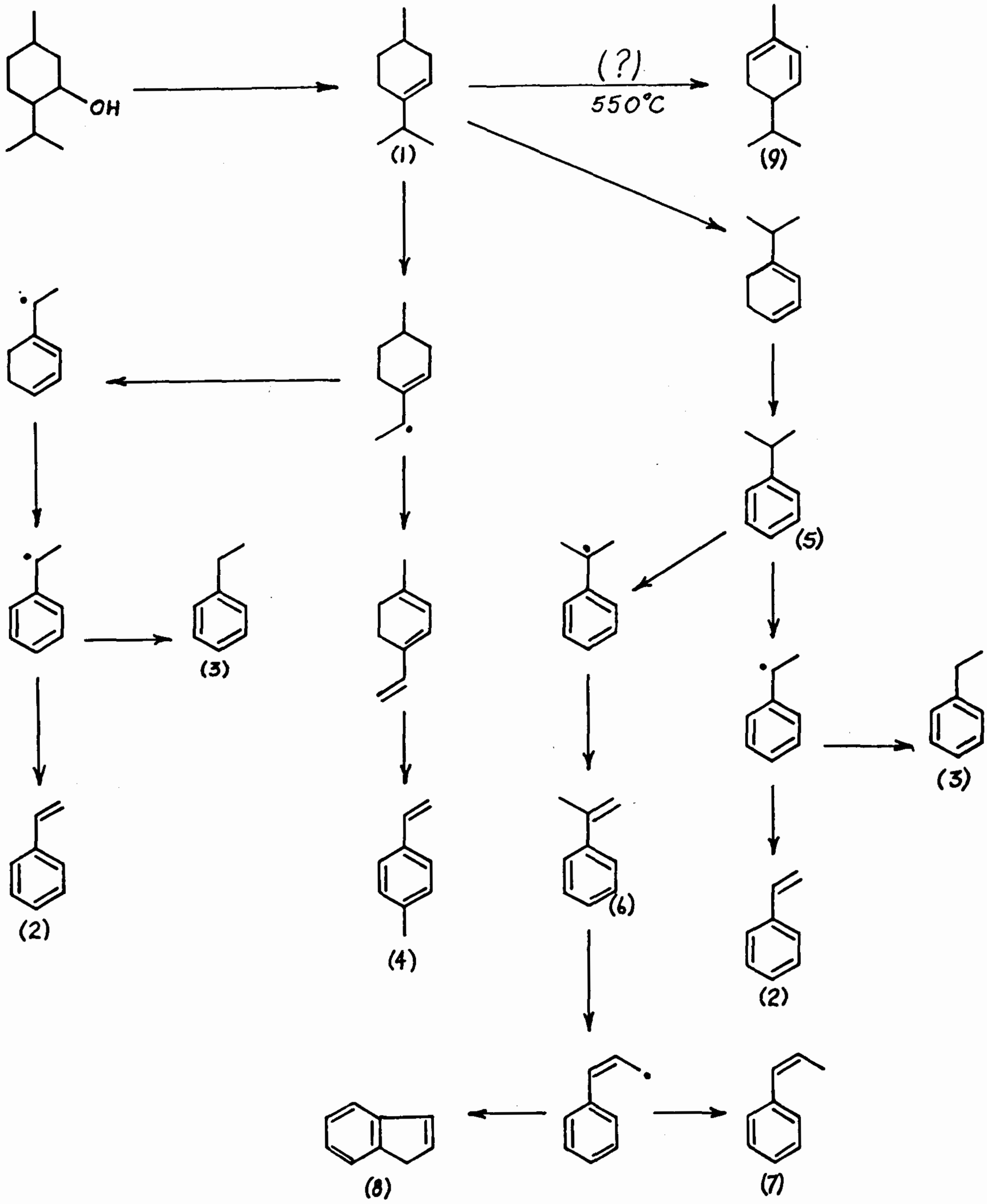


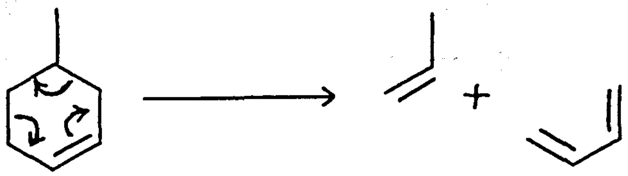
Figure VII

of menthol since both menthol and 3-p-menthene yield this compound on pyrolysis at 750°C. 2-Isopropylbutadiene-1,3, however, could only form isopropylbenzene by a diene reaction and, as shown in Table VII, produces 1/20 the amount found in the menthol and 3-p-menthene pyrolyzates.

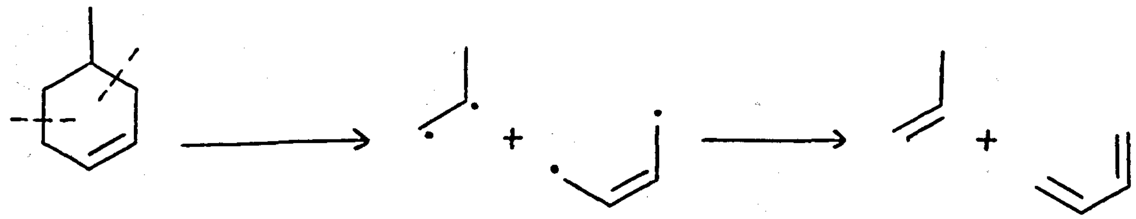
It is now appropriate to discuss the homolysis of allylic bonds in connection with the "reverse diene reaction" discussed previously. The reverse diene reaction is simply a concerted rearrangement of electrons within a molecule to produce a mono and a di olefin. It is generally a reaction which proceeds at relatively low temperatures thus requiring a fairly low activation energy (93). On the other hand, the cleavage of allylic C-H and C-C bonds to produce free radicals is also a low energy type of reaction (20, 46) but requires slightly higher temperatures.

Consider the thermal decomposition of 4-methylcyclohexene to produce butadiene and propene. This reaction may proceed by two pathways as follows;

(1)



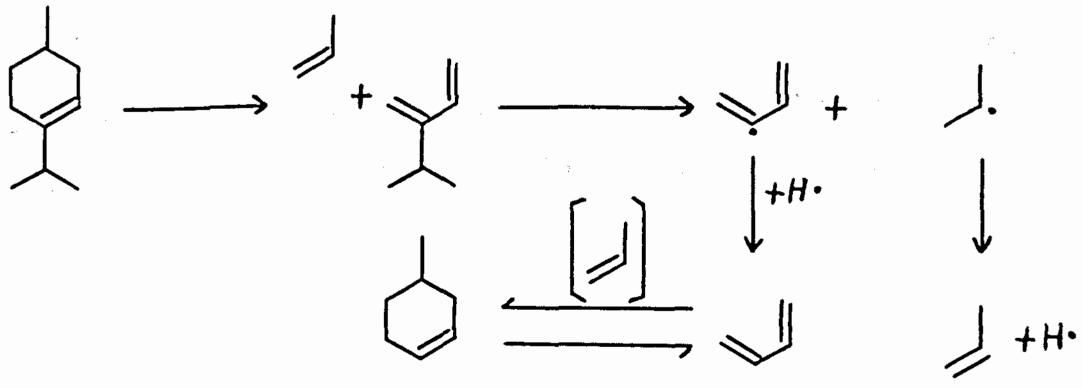
(2)



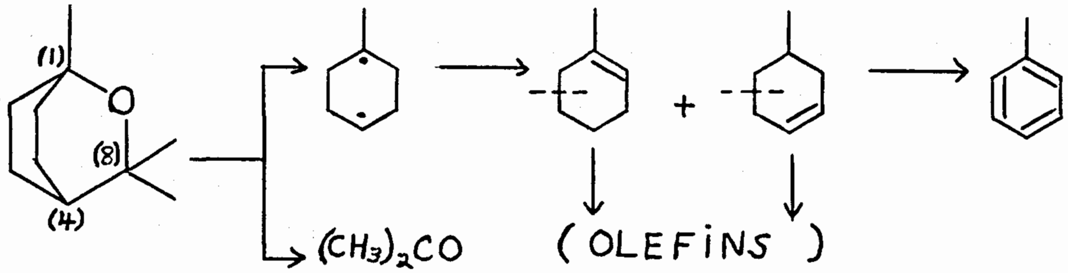
A reaction such as (2) could probably occur and proceed through a di radical which instantly attacks an alpha double bond. This di radical, however, could conceivably react with another molecule or fragment before the intramolecular attack on the double bond occurs, but this would require a suitable collision. The formation of butadiene as written would be more direct. This mechanism of decomposition is simply an extension of the reverse diene reaction since the products formed from the di radical would be essentially the same as those from butadiene.

Additional comment is necessary on the formation of 4-methylcyclohexene. One of the mechanisms by which this compound is formed during menthol pyrolysis was proposed in Figure IV. This compound is probably the primary source of butadiene via the reverse diene reaction and cleavage of allylic bonds at high temperatures.

It is interesting, however, that 4-methylcyclohexene is also formed from the pyrolysis of 3-p-menthene and 2-isopropylbutadiene-1,3, respectively, at 750°C in nearly equal concentrations. 4-Methylcyclohexene probably forms by the diene reaction in the pyrolvsis of these compounds as follows;



The only analogous decomposition of a C_{10} terpene compound to produce 4-methylcyclohexene is that reported by Hayashi (37) who pyrolyzed 1,8-cineole from 500° to 600°C. The initial cleavage and products formed were given as follows;



1-Methylcyclohexadiene was not isolated as a product of this reaction.

One of the products found by Hayashi in the pyrolysis of 1,8-cineole was p-cymene. He attributed its formation to the catalytic action of porcelain fragments used as a support.

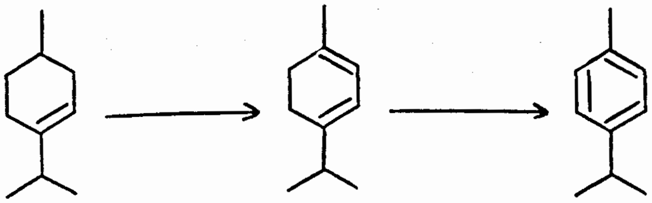
Kitajima and Noguchi (62) on the other hand pyrolyzed α-pinene, camphene, and limonene at 470°C using Japanese acid clay as a support and in no case were able to find p-cymene in the pyrolyzates. They proposed, however, that the main reaction occurring was the formation of p-cymene which instantly decomposed. If Hayashi's proposal (37) that acidic catalysts are conducive to p-cymene formation were correct, it is indeed strangethat they could not find p-cymene in the pyrolyzates using Japanese acid clay.

Pines and Ryer (87) pyrolyzed d-limonene at 450°C and found that p-cymene was the major aromatic compound produced.

The author made a careful search for p-cymene in the menthol pyrolyzates recorded in Table VII and was unable to find it. The pyrolysis of menthol from 450° to 750°C was expected to yield some p-cymene but none could be found at any of these temperatures. Two conclusions regarding p-cymene formation during the pyrolysis of menthol are possible: 1) p-cymene is not formed, and 2) if it is produced, it is thermally unstable and immediately decomposes.

Takubo and Murayama (107) pyrolyzed p-cymene vapors over bamboo charcoal from 500° to 800°C and found that p-methylstyrene and p,α-dimethylstyrene were the major products. Optimum yields were observed for p,α-dimethylstyrene at 575°-610°C and for p-methylstyrene at 650-750°C. It is not at all clear, therefore, why Hayashi (37) did not find the styrene derivatives from the pyrolysis of 1,8-cineole at 600°C since he did find p-cymene.

It is not impossible that p-cymene is a thermally unstable, transitory intermediate during the pyrolysis of menthol but it is probable that it is not produced from the following considerations: If p-cymene forms during the pyrolysis of menthol it must do so through 3-p-menthene by the following process;



Although some α-phellandrene (1,5-p-menthadiene) was observed at 550°C (Table VII), none of this compound was observed at 450°, 650°, or 750°C. A much lower energy process is available through the cleavage of an allylic C-C or C-H bond in the exocyclic isopropyl group of 3-p-menthene. When substituted cyclohexenes are pyrolyzed, alkyl groups containing more than one carbon atom are readily destroyed (93). It is also well known that C-C bonds undergo thermal rupture more easily than C-H bonds (111). If p-cymene is a key intermediate in the pyrolysis of menthol, some should be observed over the temperature range 450°-750°C. Finally, it is known that p,α-dimethylstyrene is a major product in the pyrolysis of p-cymene (107) but none was found in the menthol pyrolyzates.

F. Extended Cyclization

The formation of naphthalenes and polycyclic aromatic hydrocarbons has been studied recently by Badger and co-workers (1-8).

Staudinger, et al. (103) observed that butadiene yielded a tar at 800°C of which 30.6% was benzene and 25% was naphthalene. Jones (57) and others (36, 98, 120) followed, stressing the idea that conjugate unsaturation rather than acetylene was the necessary precursor of the naphthalenes and polynuclear hydrocarbons.

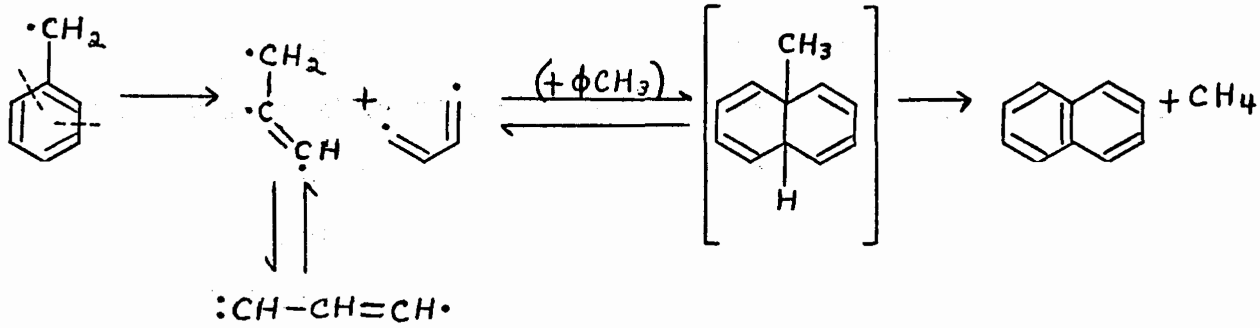
Wheeler and Wood (121) extended this idea. From olefins (C_2H_4, C_3H_6, C_4H_8) at 500°-700°C they found cyclohexene as well as benzene. Others extended the diene reaction hypothesis (36, 98) to include naphthalene formation.

Several detailed studies on the pyrolysis of butadiene have been made (8c, 26, 76, 108). Murphy and Duggan (76) and Badger and Spotswood (8c) observed naphthalene as a major product. Styrene was also a product of butadiene pyrolysis which Badger and Spotswood postulated was formed from the dimer of butadiene; 4-vinylcyclohexene.

Badger and Novotny (7a) pyrolyzed 4-vinylcyclohexene at 700°C and obtained essentially the same product mixture and respective yields as found in the pyrolysis of butadiene (8c). They postulated an extensive free radical mechanism to explain the products obtained.

Evidence of the free radical nature of naphthalene formation during the pyrolysis of organic hydrocarbons is illustrated by the pyrolysis of methyl-, ethyl-, n-propyl, and n-butyl benzenes, respectively, at 700°C (8b). Naphthalene was formed in each case and accounted for 21% of the pyrolyzate obtained from n-butylbenzene. Badger and Spotswood further illustrated the importance of free radicals and butadiene in the formation of naphthalenes by pyrolyzing 1-phenylbutadiene-1,3 at 700°C (8a). 67.2% of the pyrolyzate was naphthalene.

Hurd, et al. (47-50) have recently extended the participation of free radicals in naphthalene formation by postulating a butadiene di radical formed by thermal scission of benzyl. This intermediate is used to explain the products obtained from the pyrolysis of toluene at 825°C as follows;



Although this mechanism appears straight forward, the benzyl radical is resonance stabilized and is reported to be quite stable to extensive thermal rupture of the aromatic ring up to 1100°C (53b). Because Badger and Spotswood (8b) used a temperature of 700°C, the decomposition mechanism proposed by Hurd, et al. is not applicable to their work nor to the pyrolysis of menthol at 750°C. It is quite noteworthy, however, that Hurd, et al. postulate a butadiene di radical as the key intermediate in the formation of naphthalene.

It is probable, therefore, that the naphthalenes occurring in the pyrolyzates of menthol at 650° and 750°C are formed by the reaction of cyclohexenes and cyclohexadienes with C_4 and C_5 conjugated dienes followed by dehydrogenation and dealkylation. A second process probably occurring simultaneously and becoming more prominent at 750°C is the reaction of C_4 and C_5 unsaturated mono and di radicals with cyclohexenes and cyclohexadienes to yield naphthalenes by dehydrogenation and dealkylation.

The higher molecular weight products which consist primarily of polynuclear hydrocarbons were not investigated in this study since the primary objectives were to determine the lower molecular weight products and make a reasonable postulation of their mechanism of formation. From this information one might then propose the initial reactions occurring during the pyrolysis of menthol. The reader is referred to the work of Badger, et al. (1-8) for a more detailed and extended discussion of polynuclear hydrocarbon formation.

SUMMARY

Menthol has been pyrolyzed between 450° and 750°C and the products identified and determined. The products were separated, detected and determined using gas chromatography. Identification of the products was made using retention-time data in conjunction with mass spectroscopy and infrared and ultraviolet spectrophotometry.

The major reactions involved which constitute the preferred routes of decomposition have been postulated based on a comparison of the results with previously reported work. They are: 1) dehydration of menthol to 2-and 3-p-menthene followed by isomerization and reverse diene synthesis to 2-isopropylbutadiene-1,3 and isoprene, 2) direct cleavage of hydroxyl and isopropyl groups to produce 4-methylcyclohexene, 3) cleavage of the carbon-carbon bond alpha to the hydroxyl group, 4) isomerization of methyl radicals to produce low molecular weight mono and di olefins, 5) recombination by diene synthesis followed by dealkylation and dehydrogenation, 6) direct deakylation and dehydrogenation of 3-p-menthene to produce substituted benzene derivatives and styrenes, 7) cleavage

of allylic bonds, and 8) extended cyclization to produce naphthalenes by reaction of conjugated dienes and their corresponding di radicals with cyclohexenes and cyclohexadienes followed by dehydrogenation and dealkylation.

The pyrolyses of 2-isopropylbutadiene-1,3,3-p-menthene, and menthol, respectively, yield essentially the same product mixture at 750°C.

Additional evidence for the "wandering methyl radical" phenomenon proposed by Hurd, et al. (47) has been obtained from the pyrolysis of α-and β-methyl styrenes, respectively, at 750°C.

Contrary to results reported in the literature on pyrolysis of C_{10} monocyclic terpenes, p-cymene does not appear to play an important role in the thermal decomposition of menthol.

Acetylene does not appear to contribute to or enter into the pyrolysis reactions of menthol.

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