50 ml. of 0.4 *N* potassium hydroxide (80% ethanol) and the solution was refluxed for 4 hours. The cooled solution was extracted twice with 200-ml. portions of ether and the ether extracts washed with water, combined and dried over sodium sulfate. Concentration of the ether solution yielded 16 mg. (92%) of crystalline material which melted at 209–210°, after recrystallization from ethanol. A mixture of this product and authentic 11-ketorockogenin (Xa), melted at 209–210°. The infrared spectrum of the isolated Xa was identical with that of a standard sample.

Reaction of Methyl 3α,11β-Diacetoxy-12-ketocholanate (I) with Zinc–Acetic Anhydride.—One hundred twenty-two mg. of I was refluxed for 20 hours in 75 ml. of acetic anhydride containing 12 g. zinc dust. On cooling, the mixture was added to cold aqueous methanolic sodium hydroxide solution and filtered after 1 hour. The filtrate was extracted three times with 200-ml. portions of ether and the ether solution was washed with dilute alkali, water and dried over sodium sulfate. Concentration of the solution afforded an oil which was chromatographed on 20 g. of silica gel. Two substances were eluted in petroleum ether–ether (4:1). The first material, 35 mg. (32%), was shown by comparison of its infrared spectrum with authentic II to be methyl 3α-acetoxy-12-ketocholanate (II). One recrystallization from methanol gave material, m.p. 150–152°, which did not depress the melting point of a known sample of II. The second crystalline substance, 51 mg., had an infrared spectrum identical with I.

Reaction of Methyl 3α,11β-Diacetoxy-12-ketocholanate (I) with Zinc–Toluene.—Seventy-five ml. of toluene and 132 mg. of I were refluxed for 20 hours with 12 g. of zinc dust. After cooling, the reaction mixture was shaken with 100 ml. of 50% glacial acetic acid and then filtered from the zinc. The filtrate was processed as in the previous experiment and afforded 130 mg. of an oil, 100 mg. of which was chromatographed on 15 g. of silica gel. From the fractions washed from the column with petroleum ether–ether (17:3), 89 mg. (89%) of the starting material I was recoverable. After one recrystallization from methanol the substance melted at 109–111°; admixture of the product with authentic methyl 3α,11β-diacetoxy-12-ketocholanate (I) showed no change in melting point. The infrared spectrum of the reaction product was indistinguishable from that of starting material. No other material was identified in the chromatogram.

Acknowledgment.—The authors are indebted to Dr. Carl Djerassi of Wayne University, and Dr. George Rosenkranz of Syntex, S. A., Mexico City, for their generous gift of dibromohecogenin acetate.

NEW YORK, N. Y.

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

Studies in the Terpene Series. XXIII.[1,2] Pyrolysis of *d*-Limonene and of Related Hydrocarbons. Mechanisms of Pyrolysis

BY HERMAN PINES AND JACK RYER[3]

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The pyrolysis of *d*-limonene and of a mixture consisting of α- and β-pyronene and of 1,5-dimethyl-5-ethyl-1,3-cyclohexadiene (V) over copper pellets at 450° and at atmospheric pressure was studied. It was found that *d*-limonene formed 9% aromatic hydrocarbons containing as the major constituents *p*-cymene, 1,2,3,5-tetramethylbenzene, *m*-xylene and trimethylbenzenes. The non-aromatic hydrocarbons contained geminal and non-geminal alkylcyclohexanes, which on dehydrogenation formed polymethylated alkylbenzenes. The mixture of pyronenes (VII and IX) and of compound V on pyrolysis formed products having composition similar to that obtained from *d*-limonene. A biradical mechanism is proposed to explain the formation of the various compounds.

Introduction

The catalytic rearrangement of terpenes and related compounds at elevated temperatures has been a subject of extensive studies in this Laboratory. Inasmuch as terpenes and certain bicyclic dihydroterpenes may undergo changes when exposed to high temperatures in the absence of catalysts it was deemed necessary to investigate the extent to which these pyrolytic reactions were responsible for the rearrangement of the terpenes studied. For that reason the pyrolysis of pinane[4a,b] and 6,6-dimethylnorpinane[5] were investigated. It was found that pinane rearranges at 400–500° to 3,7-dimethyl-1,6-octadiene and to *cis, cis, cis* and *cis, trans, cis*-1,2-dimethyl-3-isopropenylcyclopentane. Dimethylnorpinane forms similar compounds, namely, 7-methyl-1,6-octadiene and *trans*-1-methyl-2-isopropenylcyclopentane.

Of the terpenes only the pyrolysis of α- and β-pinene and of alloöcimene have been studied extensively. Fuguitt and Hawkins[6] on the basis of a kinetic study, concluded that several processes occurred simultaneously when α-pinene was heated at 200–500°. These processes included the racemization of α-pinene, isomerization to almost optically inactive limonene (dipentene) and isomerization to alloöcimene through an intermediate ocimene.[7] At higher temperatures pyronenes[8] and other cyclic hydrocarbons were produced.

The products of the pyrolytic isomerization of β-pinene were not identical with those of α-pinene. They consisted of optically active limonene and myrcene.[9]

Burwell[10] has proposed a mechanism for the pyrolysis of pinenes, involving biradical intermediates, which is in accord with all of the above indicated facts.

The pyrolysis of alloöcimene was studied by Parker and Goldblatt.[11] They found that the product contained besides α- and β-pyronene a substantial

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[1] For previous paper of this series see H. Pines and J. Maréchal, THIS JOURNAL, **77**, 2819 (1955).

[2] This work was made possible in part through the financial assistance of Universal Oil Products Company, Des Plaines, Illinois.

[3] Taken in part from the Doctoral Dissertation submitted to the Department of Chemistry, Northwestern University, Evanston, Illinois, January, 1954.

[4] (a) V. N. Ipatieff, W. D. Huntsman and H. Pines, THIS JOURNAL, **75**, 6222 (1953); (b) H. Pines, N. E. Hoffman and V. N. Ipatieff, *ibid.*, **76**, 4412 (1954).

[5] H. Pines and N. E. Hoffman, *ibid.*, **76**, 4417 (1954).

[6] R. E. Fuguitt and E. J. Hawkins, *ibid.*, **67**, 242 (1945).

[7] E. J. Hawkins and H. G. Hunt, *ibid.*, **73**, 5379 (1951).

[8] G. Dupont and R. Dulou, *Compt. rend.*, **201**, 219 (1935).

[9] L. A. Goldblatt and S. Palkin, *ibid.*, **63**, 3517 (1941).

[10] R. L. Burwell, Jr., *ibid.*, **73**, 4461 (1951).

[11] E. E. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950).

amount of 1,5-dimethyl-5-ethyl-1,3-cyclohexadiene and smaller amounts of polymethylated benzene.

In spite of the wide distribution of *d*- and *l*-limonene and of the *dl* (racemic) form, dipentene, there are only few detailed accounts of their pyrolysis. The results reported are often contradictory, owing to the impurities which were present in the investigated limonene, and to the lack of satisfactory analytical methods.[12] The formation of isoprene from dipentene, pinenes and other terpenes has been studied. No detailed composition, however, of the higher boiling hydrocarbons was given.[13]

I. Limonene

(a) Discussion of Results.—*d*-Limonene was passed over copper pellets at atmospheric pressure at 450° and at HLSV[14] of 0.4. It was previously noted that at the above indicated conditions the copper acts as an inert contacting material. The small amount of non-condensable gaseous products resulting from this reaction consisted of hydrogen, methane, ethane and ethylene. The liquid hydrocarbons contained isoprene, amounting to 6% by weight of limonene charged. The fraction boiling between 115 and 190° and amounting to 86% of the material charged was composed of 9% aromatics and 91% non-aromatic hydrocarbons; the latter were mainly diolefins since they absorbed 1.9 moles of hydrogen per mole of hydrocarbons. The residue remaining in the flask was not further investigated.

About 75% of the product boiling at 115–190° was selectively hydrogenated in the presence of copper chromite catalyst. This hydrogenation converted the unsaturated hydrocarbons to saturated ones, while the aromatics remained unchanged. The aromatic hydrocarbons, which were separated chromatographically from the saturated hydrocarbons, were distilled and identified by means of infrared spectral analysis and by solid derivatives. The composition of the aromatics is given in Table I.

TABLE I

PYROLYSIS OF *d*-LIMONENE COMPOSITION OF AROMATIC HYDROCARBONS

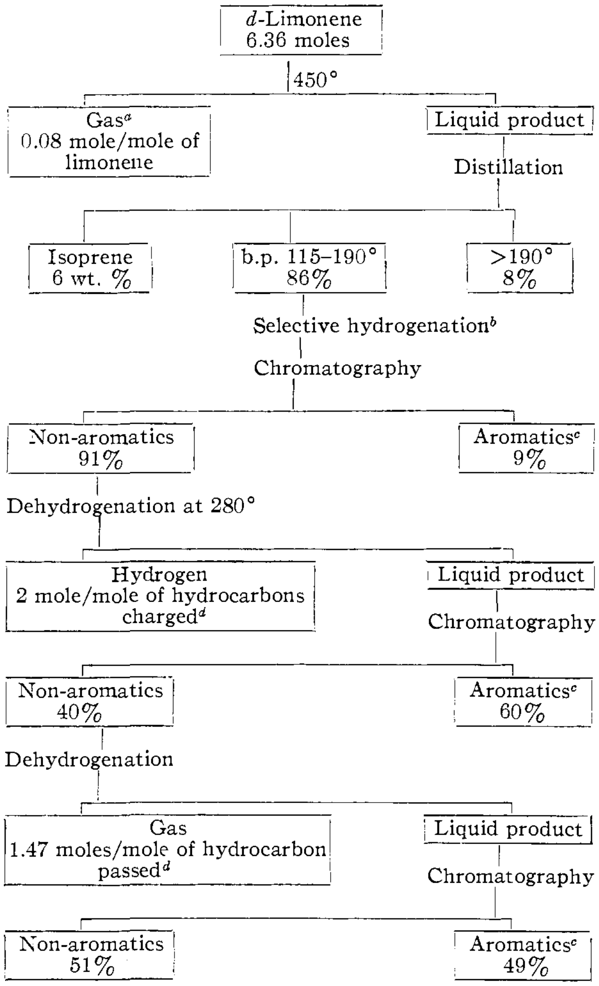
Aromatic hydrocarbons	% by weight Originally present	From dehydrogenation at 280°	330°
m-Xylene	16[a]		4
m-Ethyltoluene	3	1	38
p-Ethyltoluene	2		
1,2,3-Trimethylbenzene	6[c]		26[c]
1,2,4-Trimethylbenzene	6[b]	1	7[b]
p-Cymene	30[d]	88	12
1,3-Dimethyl-4-ethylbenzene	2		
1,3-Dimethyl-5-ethylbenzene			
1,2,3,5-Tetramethylbenzene	19[e]	2	

[a] Trinitro-*m*-xylene melted at 181°. [b] Sulfonic acid derivative melted at 103°. [c] Sulfonic acid derivative melted at 115°. [d] 2,4-Dinitrophenylhydrazone of acetylated *p*-cymene melted at 157°. [e] 4,6-Dibromoisodurene melted at 198°. *Anal.* Calcd. for $C_{10}H_{12}Br_2$: Br, 54.8. Found: Br, 55.2.

The saturated hydrocarbons, obtained from the selective hydrogenation, contained geminal and non-geminal alkylcyclohexanes. These two types of alkylcyclohexanes were separated by selective dehydrogenation using platinized alumina as a catalyst.[15] The dehydrogenation was carried out at 280°, at which temperature only the non-geminal alkylcyclohexanes were converted to the corresponding aromatic hydrocarbons. The latter amounting to 60% were separated by chromatography from the geminal saturated hydrocarbons, distilled and the various fractions analyzed by means of infrared spectroscopy (Table I).

TABLE II

PYROLYSIS OF *d*-LIMONENE. OUTLINE OF ANALYTICAL PROCEDURE



[a] Composition of gas in mole %, as determined by a mass spectrograph 18.8% hydrogen, 39.8% methane, 17.4% ethane, 15.4% ethylene, 4.7% propylene. [b] 1.9 moles of hydrogen was absorbed per mole of hydrocarbons charged. [c] Composition is given in Table I. [d] The average molecular weight of 126 (C_9H_{18}) was assumed.

The saturated hydrocarbons which did not undergo dehydrogenation at 280° and containing geminal alkylcyclohexanes were passed over the dehydrogenation catalyst at 330°. At this temperature

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[12] For the review of literature see G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1937.

[13] B. L. Davis, L. A. Goldblatt and S. Palkin, *Ind. Eng. Chem.*, **38**, 53 (1946).

[14] Hourly liquid space velocity or volume of liquid per volume of pellets per hour.

[15] H. Pines, R. C. Olberg and V. N. Ipatieff, THIS JOURNAL, **70**, 533 (1948).

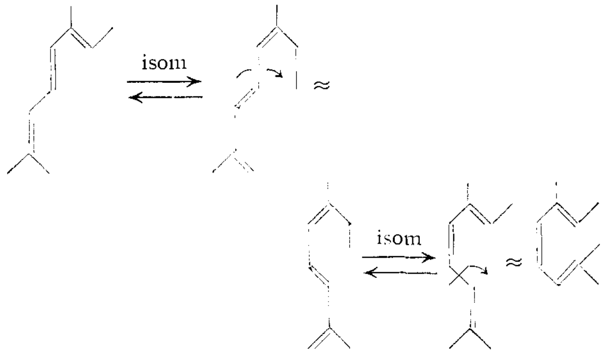
the geminal alkylcyclohexanes undergo dehydrogenation with a loss of an alkane, while alkylcyclopentanes and bicyclic hydrocarbons which do not contain either three or four-membered rings remain unchanged.[16] The gases obtained from the dehydrogenation reaction were composed of hydrogen, methane and ethane. The aromatic hydrocarbons contained as the major products *m*-ethyltoluene and 1,2,3- and 1,2,4-trimethylbenzene (Table I). The presence of *p*-cymene is due to a non-completed dehydrogenation at 280° of *p*-menthane.

The procedure used for the determination of the various types of hydrocarbons formed and the results obtained are presented schematically in Table II.

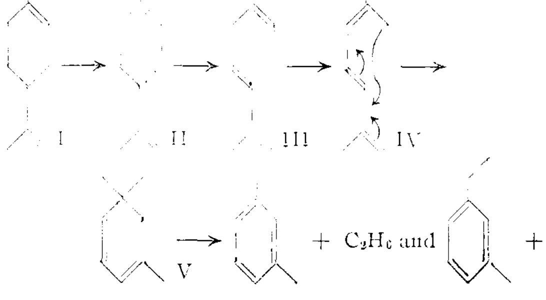
On the basis of the analytical results obtained it was calculated that the non-aromatic hydrocarbons, b.p. 115–190°, obtained from the pyrolysis of *d*-limonene were composed of 54% dipentene or its double bond isomers, 13% of geminal alkylcyclohexanes, 9% of non-geminal alkylcyclohexanes and 19% of alkylcyclopentanes and bicyclic hydrocarbons.

The effect of temperature on *d*-limonene was also studied. At 415° and at 0.4 HLSV most of the limonene was recovered essentially unchanged. At 500°, however, extensive decomposition occurred and the copper pellets were coated with carbon.

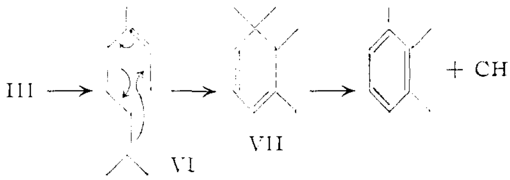
(b) **Proposed Mechanism. 1. Aromatic Hydrocarbons.**—The various polyalkylated benzenes obtained from the pyrolysis of *d*-limonene (I) may be explained as involving an internal cleavage of the carbon–carbon bond at the allylic position, giving rise to a biallyl biradical (II). By intramolecular hydrogen transfer a triolefin III is obtained, which can then isomerize to a conjugated triolefin IV. This conjugated triolefin can cyclize by an intramolecular diene synthesis,[17] which may involve a concerted mechanism, to give rise to 1,5-dimethyl-5-ethylcyclohexadiene (V)[a]. Cyclization of a triolefin to a cyclic diolefin can occur only if the triolefin is in a cisoid form. For that reason a cisoid triolefin must rearrange to the transoid form before cyclization can occur. This rearrangement can be illustrated as follows, using *trans*-alloöcimene as an example.



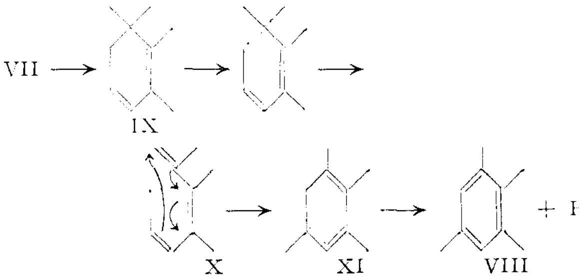
This triolefin is an intermediate postulated by Parker and Goldblatt[11] in the thermal cyclization of alloöcimene (VI) to compound V. The latter may form *m*-xylene by a loss of ethane and *m*-ethyltoluene by loss of methane. The following scheme illustrates the proposed mechanism



The formation of 1,2,3-trimethylbenzene can be explained by a similar sequence of reactions. The triolefin III through an isomerization to alloöcimene (VI) can form α-pyronene (VII), as previously reported.[11] The latter loses methane to form the trimethylbenzene.

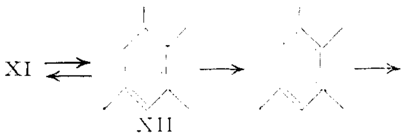


The presence of a large proportion of 1,2,3,5-tetramethylbenzene (isodurene) (VIII) as the only tetramethylbenzene detected in the aromatic fraction can be explained by the isomerization of α-(VII) to β-pyronene (IX) followed by the cleavage of the latter through a biallyl biradical to a trimethylheptatriene (X), which by a cyclization may yield 1,2,3,5-tetramethylcyclohexadiene (XI). The latter hydrocarbon was found in the products of the thermal reaction of alloöcimene.[11] Compound XI by a loss of hydrogen forms isodurene (VIII).



The conversion of α- to β-pyronene by pyrolysis in the liquid phase was noticed previously.[11]

The presence of 1,2,4-trimethylbenzene can be interpreted by the internal cleavage of XII to a biallyl biradical. The following scheme represents the various steps which seem to be involved in this reaction



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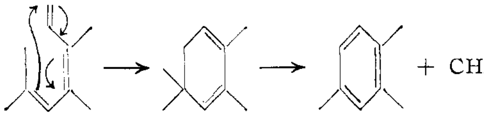
[16] V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **68**, 1709 (1946).

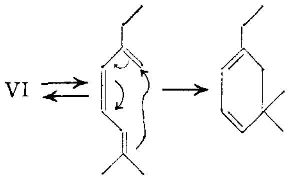
[17] K. Alder and M. Schumacher, "Anwendungen der Dien-Synthese für die Erforschung von Naturstoffen" in "Progress in the Chemistry of Organic Natural Products," Springer Verlag, Wien, 1953, pp. 10, 52.



XIII XIV

2. Geminal Alkylcyclohexanes.—The geminal alkylcyclohexanes obtained from the hydrogenation of the corresponding unsaturated hydrocarbons, which consisted mainly of terpenes ($C_{10}H_{16}$), yielded on dehydrogenation aromatic hydrocarbons (Table I), methane or ethane, and hydrogen. It was found that of the geminal alkylcyclohexanes present 72% liberated methane and 28% ethane on dehydrogenation.

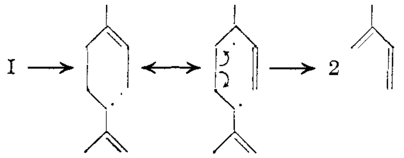
m-Xylene was most probably formed from the dehydrogenation of the hydrogenated compound V, while *m*-ethyltoluene was predominantly formed from the originally present 1,1-dimethyl-3-ethyl-3,-5-cyclohexadiene (XVI). This conclusion is based on the observation made previously[1] that 1-methyl-1-ethylcyclohexane on dehydrogenation under similar conditions as used in this investigation yielded equal amounts of toluene and ethylbenzene. It can, therefore, be concluded that the concentration of the hydrogenated compound V in the geminal alkylcyclohexane fraction cannot exceed 8%, while the concentration of 1,1-dimethyl-3-ethylcyclohexane, hydrogenated compound (XVI), was at least 36%. The source of the latter compound was most probably compound (VI)



XV XVI

The presence of 1,2,3- and 1,2,4-trimethylbenzene is due to the pyronenes (VII and IX) and to compound (XIV).

3. Isoprene.—The formation of isoprene from *d*-limonene can likewise be explained by the initial formation of a biallyl biradical, followed by allylic rearrangement and β-scission



II. Pyronenes and 1,3-Dimethyl-1-ethyl-3,5-cyclohexadiene (V)

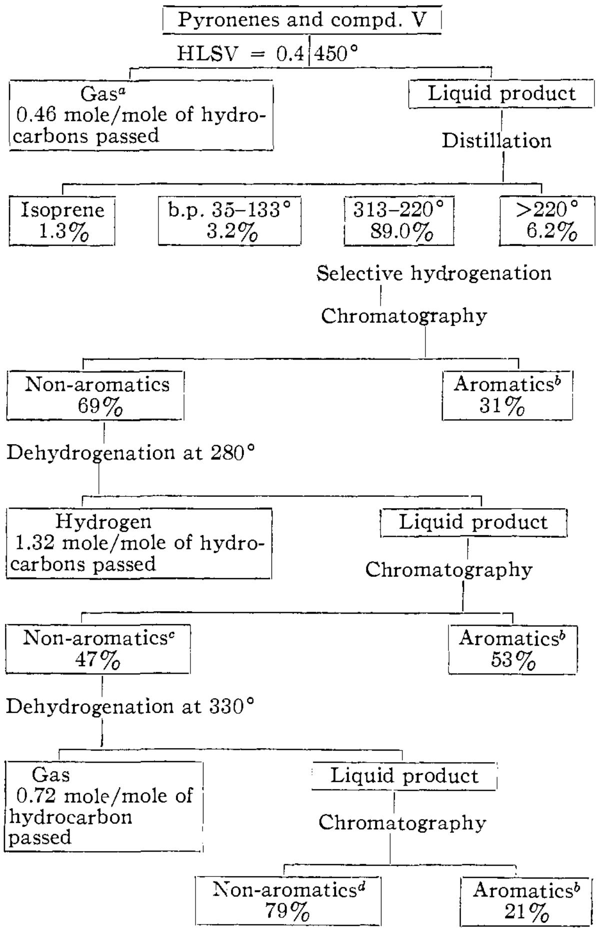
a. Discussion of Results.—It was shown above that the pyrolysis of *d*-limonene yielded a mixture of hydrocarbons. The presence of some of these hydrocarbons was interpreted by an intermediate formation of α- and β-pyronene and compound V. In order to shed additional light upon the mechanism of pyrolysis of limonene, it was of interest to study the pyrolysis of these compounds and to compare the products formed with those obtained from limonene.

When a mixture of pyronenes and compound V was pyrolyzed over copper pellets at 450° and at HLSV of 0.4, gaseous and liquid hydrocarbons were formed. The gases which amounted to 0.46 mole per mole of terpenes passed consisted of 54% methane with smaller amounts of hydrogen, ethane and ethylene. The liquid product contained about 2% of isoprene, 89% of material boiling between 133 and 220° and the remainder of higher and lower boiling hydrocarbons.

The fraction boiling at 130–220° was analyzed by means of selective hydrogenation, chromatography and selective dehydrogenation (Table III). This fraction was found to be composed after selective hydrogenation of 31% aromatic hydrocarbons, 38% of non-geminal and 6% of geminal-alkylcyclohexanes and the remainder probably of alkylcyclopentanes. The composition of the aromatic hydrocarbons originally present in this fraction and those obtained from the selective dehydrogenation is summarized in Table IV. The presence of 1,3-dimethyl-4-ethylbenzene in the products of the dehydrogen-

TABLE III

PYROLYSIS OF MIXTURE OF PYRONENES AND OF 1,3-DIMETHYL-1-ETHYL-3,5-CYCLOHEXADIENE. OUTLINE OF ANALYTICAL PROCEDURE



[a] Composition of gases as determined by mass spectrograph: 15% hydrogen, 54% methane, 19% ethane, 6% ethylene. [b] The composition of the aromatic hydrocarbons is given in Table IV. [c] *Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.9; H, 14.4. [d] *Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.4; H, 14.3.

ation at 330° is due probably to a non-complete dehydrogenation of the corresponding alkylcyclohexanes at 280°.

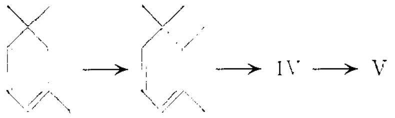
TABLE IV

PYROLYSIS OF A MIXTURE OF PYRONENES AND OF COMPOUND V. COMPOSITION OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons	% by weight Originally present	From the dehydrogenation at 280°	330°
m-Xylene	30		15
m-Ethyltoluene	7	4	30
p-Ethyltoluene			7
1,2,3-Trimethylbenzene	16		25
1,2,4-Trimethylbenzene	7	4	8
1,3,5-Trimethylbenzene		3	9
1,3-Dimethyl-4-ethylbenzene	8	16	7
1,2,3,5-Tetramethylbenzene	17	36	

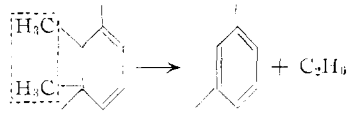
b. Proposed Mechanism.—The hydrocarbons obtained from the pyrolysis of pyronenes and 1,3-dimethyl-1-ethylcyclohexadiene (V) resemble those obtained from limonene. This was not unexpected since in the proposed mechanism of the pyrolysis of limonene it was suggested that the above terpenes were the intermediate products in the formation of some of the hydrocarbons. It is not surprising therefore that the yields of 1,2,3-trimethylbenzene and that of 1,2,3,5-tetramethylbenzene (VIII) and of the corresponding tetramethylcyclohexadiene (XI) were relatively high. Their mechanism of formation was already discussed.

The presence of *m*-xylene in the original aromatic fraction or in that produced from the dehydrogenation at 280° was probably due to a great extent to compound V present in the charge. It is, however, not excluded that compound V might also have been formed from the pyrolysis of α-pyronene according to the scheme



VII XVII

It was reported by Dupont and Dulou[18] that pyronenes are transformed at about 400° into *m*-xylene with the evolution of ethane. They suggested, however, that ethane was produced by the condensasation of two methyl groups, according to the scheme

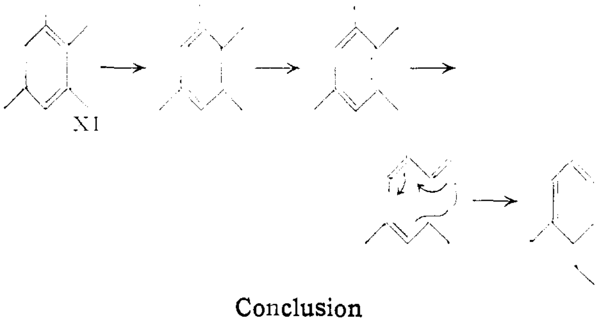


This mechanism appears to be unlikely, since methane and 1,2,3-trimethylbenzene would have resulted from a direct splitting of a methyl group from α-pyronene.

m-Ethyltoluene, which was obtained from the dehydrogenation reaction made at 330°, was most likely derived from compound XVI rather than from V. This conclusion is based on the fact that *m*-xylene was not formed during the dehydrogenation as it would have been expected from compound V. The formation of XVI from α-pyronene can be explained by the following series of reactions

$$\text{VII} \rightarrow \text{XVII} \rightarrow \text{IV} \rightarrow \text{XV} \rightarrow \text{XVI}$$

The presence of 1,3-dimethyl-4-ethylbenzene in the aromatic fraction originally present or in that produced on dehydrogenation of alkylcyclohexanes can be explained by the isomerization and pyrolysis of the tetramethylcyclohexadiene (XI)



XI

Conclusion

It was observed that the pyrolysis of limonene and of a mixture of hydrocarbons containing pyronenes and compound V yielded products composed of aromatic and non-aromatic cyclic hydrocarbons. The formation of the various compounds was explained on the basis of the formation of biallyl biradicals, which by an internal hydrogen transfer reaction can be converted either directly or by a two-step process to conjugated triolefins. The latter by means of an intramolecular diene synthesis, which may involve a concerted mechanism, forms conjugated alkylcyclohexadienes. The alkycyclohexadienes may: (a) remain unchanged; (b) be converted to the corresponding aromatic hydrocarbons by loss of methane, ethane or hydrogen or (c) may undergo cleavage to form new biallyl biradicals, which again may undergo the same type of changes as indicated above.

Experimental Part

Apparatus.—The apparatus consisted of a Pyrex reaction tube of 21 mm. outside diameter heated by a thermostatically controlled vertical furnace. The terpenes were introduced into the reaction tube, packed with 50 cc. of $^1/_8$ inch copper pellets, by means of a liquid feed pump. The lower end of the reaction tube was attached to a liquid receiver, which in turn was attached through an ice and Dry Ice–acetone cooled trap into a gas measuring and sampling bottle.

The lower boiling monomeric material was separated from the high boiling product by means of distillation, which was made under reduced pressure on a "Hypercal" column.[19]

The procedure used for the determination of the various hydrocarbons is given in Tables II and IV.

The fractional distillation of aromatic hydrocarbons obtained from the chromatographic separation was made on a Piros-Glover spinning band column.[20]

Analytical Procedures. Selective Hydrogenation.—The hydrocarbons were dissolved in equal volumes of *n*-pentane and hydrogenated in the presence of 10–15% by weight of copper chromite catalyst.[21] The hydrogenation was carried out in a 450-ml. rotating autoclave at 100° and in the presence of 100 atmospheres of initial hydrogen pressure. The degree of unsaturation was calculated from the drop in pressure.

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[18] G. Dupont and R. Dulou, *Bull. soc. chim. France*, C29-35 (1951).

[19] Podbielniak, Inc., Chicago, Illinois.

[20] Manufactured by H. S. Martin and Company, Evanston, Illinois.

[21] W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 142.

Chromatographic Separation.—The aromatic hydrocarbons were separated from the non-aromatic hydrocarbons by means of silica gel.[22] The aromatic portion was distilled and the composition of the various fractions determined by means of infrared spectral analysis and solid derivatives.

Dehydrogenation.—The non-geminal alkylcyclohexanes present in the saturated hydrocarbon portions were dehydrogenated at 280° to the corresponding aromatic hydrocarbons using platinum–alumina as a catalyst.[15] The aromatic hydrocarbons thus produced were separated chromatographically. The non-aromatic hydrocarbons remaining and containing geminal alkylcyclohexanes were dehydrogenated at 330°,[16] and again chromatographed. The aromatic hydrocarbons separated from each of the dehydrogenation reactions were distilled separately on a spinning band column and each fraction analyzed by means of infrared spectrography.

Identification of Aromatic Hydrocarbons.—2,4,6-Trinitro-*m*-xylene,[23a] 1,2,4-trimethylbenzene-5-sulfonic acid[23b] and 1,2,3,5-tetramethyl-4,6-dibromobenzene were prepared by standard procedures.

p-Cymene was separated from the trimethylbenzenes by sulfonation using a similar procedure to that outlined by Smith and Cass.[24] *p*-Cymene under the conditions used did not undergo sulfonation, whereas the trimethylbenzenes formed solid sulfonic acid derivatives. The *p*-cymene thus obtained was acetylated and converted to a solid 2,4-dinitrophenylhydrazone.[25]

Materials. *d*-**Limonene.**—It was separated by distillation from crude limonene, obtained from orange oil.[26] The *d*-limonene used for investigation distilled at 174–175°, n^{20}_{D} 1.4722, α^{20}_{D} +93.

Mixture of Pyronenes and Compound V.—It was prepared by the pyrolysis of alloöcimene. The latter was obtained in 22% yield by the pyrolysis of pinene according to the method of Goldblatt and Palkin.[27] The alloöcimene fraction distilled at 63–68° at 7 mm.; n^{20}_{D} 1.5440.

The pyrolysis of alloöcimene was made at 430°, according to the general procedure of Parker and Goldblatt.[11] The pyrolysate was distilled and a fraction boiling at 42–59° at 6 mm., n^{20}_{D} 1.4760 and representing 68% of the total was separated and used for the pyrolytic study. This fraction consisted according to the boiling point and physical constants of approximately 15% α-pyronene, 15% compound V and 70% β-pyronene.

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EVANSTON, ILLINOIS

[Contribution from the Purdue Research Foundation and Department of Chemistry, Purdue University]

Chemistry of Hexachlorocyclopentadiene. III. Synthesis of Bis-(pentachlorocyclopentadienyl) and Related Compounds[1,2]

By E. T. McBee, J. D. Idol, Jr., and C. W. Roberts

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The reaction of hexachlorocyclopentadiene (I) with cuprous chloride in 80% ethanol at 25° gives bis-(pentachlorocyclopentadienyl) (IIa). The assignment of the structure of IIa is supported by its ultraviolet absorption spectrum and by reduction to bicyclopentyl. IIa fails to form Diels–Alder adducts, but adds one mole of chlorine giving a dimer of I assumed, on the basis of its pyrolysis to I, to be perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (III). III is rearranged by aluminum chloride to the isomer, m.p. 485° (V). Exhaustive chlorination of bicyclopentyl gives a compound $C_{10}Cl_{14}$ (IV), the carbon skeleton of which is established by reduction to bicyclopentyl.

Discussion

The reductive coupling of compounds possessing allylic halogen atoms by copper powder, cuprous chloride and hydrogen over palladium has received the attention of previous investigators.[3,4]

Cuprous chloride in 80% ethanol at 25° with hexachlorocyclopentadiene (I) results in the formation of a solid compound, $C_{10}Cl_{10}$ (II), in 73% yield. Compound II is also obtained both from I and copper–bronze powder in refluxing petroleum ether (b.p. 90–100°) and by passing hydrogen at atmospheric pressure into a solution of I in toluene in the presence of a palladium-on carbon catalyst.[5]

The infrared spectrum of II in carbon tetrachloride establishes the absence of hydrogen and shows certain similarities to that of I (Table I), while molecular weight determination establishes that the material is dimeric in nature.

Table I

Infrared Absorption Bands for Hexachlorocyclopentadiene and Bis-(pentachlorocyclopentadienyl) (II)

C_5Cl_6 bands, μ	$C_{10}Cl_{10}$ bands, μ
6.25	6.28
8.15	8.18
10.39	10.35
12.35–55	12.35

Classical zinc–acid and zinc–ethanol dehalogenation methods failed to give stable, easily isolable derivatives of II. However, low pressure hydrogenation using a platinum–iron catalyst resulted in the uptake of fourteen moles of hydrogen to give a compound $C_{10}H_{18}$. The use of iron as a cocatalyst halved the reaction time but did not otherwise influence the course of reaction or the nature of products. When glacial acetic acid was used as the hydrogenation solvent, only four moles of hydrogen

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