The watch glass is now removed and the heat regulated until there is a slow evolution of sulfuric acid fumes. This heating is continued until all of the acid has been expelled. A grayish residue generally results. The crucible is then heated slowly by means of a small direct flame until the evolution of white fumes has practically ceased. A more intense heat is then applied, finally ending with ignition by a Méker burner. The crucible and contents are ignited to constant weight and the tin is estimated as stannic oxide.

The results of some representative analyses follow.

TABLE I

RESULTS OF ANALYSES

	Sn, %		
Compound	Calcd.	Found	
Tetraethyl tin	50.53	50.66, 50.30	50.54, 50.13
Tetra-*n*-butyl tin	34.21	34.06	34.02
Tri-*n*-butyl tin bromide	32.14	32.39	32.26
Di-*n*-butyl tin dibromide	30.22	29.81	29.99
Triethyl-*p*-bromophenyl tin	32.81	32.33	32.12
Tetraphenyl tin	27.80	27.85	27.95
Triphenyl tin iodide	24.89	24.60	24.82
Triphenyl-*p*-chlorophenyl tin	25.72	25.81	25.74

The authors wish to acknowledge some check analyses carried out by C. C. Vernon and W. L. Wall.

Summary

A method has been described for the quantitative estimation of total tin in a variety of organotin compounds. The method consists of a preliminary decomposition by bromine in carbon tetrachloride followed by a nitric–sulfuric acid oxidation to stannic oxide.

AMES, IOWA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. I. PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF NATURAL RUBBER

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

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The destructive distillation of rubber has been studied by many investigators. Isoprene and dipentene have been isolated many times, identified and shown to be the predominating products. The existence of other products has often been detected and empirical names have been given to them. Ipatiew and Wittorf[1] have positively identified trimethylethylene; Harries[2] identified myrcene and also a terpene with a boiling point of 168–169°. Heveen (b. p. 252°) was found by Bouchardat[3]

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[1] Ipatiew and Wittorf, *J. prakt. Chem.*, **55**, 2 (1897).

[2] Harries, *Ber.*, **35**, 3662 (1902).

[3] Bouchardat, *Bull. soc. chim.*, **24**, 108 (1875).

and Staudinger[4] recently, has isolated two compounds which he believes to be dimethylbutadiene and tetrahydrotoluene. Staudinger and associates[4,5] also state that in the distillate from destructive distillation at reduced pressure only isoprene and dipentene are present in the fraction below 200°.

The present work was undertaken largely for the purpose of throwing light upon the structural formula of the rubber hydrocarbon and, although this objective has not been attained, it is hoped that an extension of the methods of prediction developed herein to the constitution of heveen, $C_{15}H_{24}$, may eventually yield constructive results.

Procedure

Two hundred pounds of light pale crepe were destructively distilled at atmospheric pressure, in 16-lb. batches in an iron vessel connected to a suitable condensing system. No attention was paid to temperature control, due to the large size of the batches; the temperature was always raised as quickly as possible to about 700°, in order to obtain a favorable yield of isoprene, which was desired for work on synthetic rubber. The distillate is a dark-colored oil. After removal of isoprene by fractionation, the residual oil was subjected to thorough fractional distillation in a carborundum-coated spiral column.[6] Cuts were made for every degree between 50 and 176°. The customary volume of an intermediate was 5 cc., except where components were detected within 4° of each other, in which case the intermediates were larger. Several components were present to the extent of 50 cc. or more, and in such cases accurate and positive identification could be made. In other instances, 10 or 15 cc. was the maximum amount to work with. Such cases are recorded in the data only when the identification was sufficient to be certain of the series to which the component belonged.

It was later discovered that the addition of magnesium to the rubber greatly increased the yield of materials other than isoprene and dipentene. Zinc, iron and aluminum have a similar effect but to a very much smaller extent; copper is without effect; brass equals iron. A batch of 16 lb. of rubber was destructively distilled in the presence of 850 g. of magnesium and the product separately investigated. The same components were found that had been identified in the distillation of rubber alone but the proportions were different. The material from the distillation with magnesium is richer in compounds of the aromatic series and poorer in chain compounds. The liberty has been taken only in the cases of a few of the chain compounds, which were present in both cases in extremely

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[4] Staudinger, *Helv. Chim. Acta*, **9**, 549 (1926).

[5] Staudinger, *ibid.*, **9**, 529 (1926).

[6] T. Midgley, *Ind. Eng. Chem.*, **20**, April (1929).

small quantity, of combining the same cuts in order to obtain a sufficient sample to work with.

Wherever two or more components could not be separated to purity by fractional distillation, other methods of purification were used. Distillation from aniline proved to be very useful in separating chain from hydro-aromatic compounds. Compounds of the aromatic series were treated with bromine to eliminate the ethylenic impurities and steam distilled.

Cuts were considered suitable for identification: (1) when the Engler distilling range was less than 2°, (2) when special tests gave positive identification of the presence of a compound in the bulk, (3) when the compounds present could each be identified separately and the physical properties of the mixture checked this analysis (this has been done in only one case when more than two compounds were present) or (4) when continued purification failed to alter the physical properties.

In general, physical constants were relied upon for identification. These were augmented by titration of the unsaturation with a KBr–$KBrO_3$ mixture and by determination of the molecular weight. Quantitative hydrogenation with platinum black, followed by removal of the aromatic compounds by nitration, played an important part in many identifications. Special tests were used when found in the literature. Combustion was used in cases where the C–H ratio was in doubt.

Due to the small quantity of hydrocarbon left after other methods of identification had been exhausted, the location of double bonds with potassium permanganate was rendered impracticable. Consequently, where the comparison of physical constants is not sufficiently accurate to locate a double bond or where the constants are lacking in the literature, the exact position of the double bond remains in doubt. The location is actually being determined by ozonation and will be reported later.

In addition to the components which could be separated by fractional distillation, a substantial proportion of the original material polymerized, remaining as a jelly in the distilling flask. It may be safely assumed that the materials lost in this way consisted very largely of dienes which were too unstable to distil.

Results

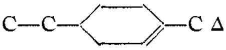
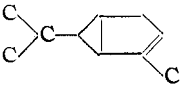
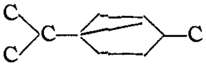
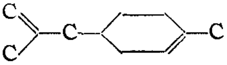
Briefly stated, the materials found were olefinic, dienic, aromatic and hydro-aromatic compounds, and a single dicyclic olefin. No fully saturated compound was detected. Table I lists the names of the compounds, the degree of accuracy of their identification and the relative quantities present in the two types of distillates.

The following paragraphs describe more completely each compound listed in the table. The common or Geneva name is used to initiate the paragraph when positive identification has been secured. It is followed by the physical constants from "International Critical Tables" (abbreviated as I. C. T.) or other sources, which are then indicated. The next listed item is the method of purification, followed by the physical constants of the purified substance. Additional data include special tests, constants of the hydrogenated compounds, special observations, etc. Where no positive identification is possible, the paragraph is headed by the word COMPONENT, followed by the physical constants found and any other data bearing on the partial identification. The boiling point ranges refer to Engler distillation from the ten-to-ninety-per cent.-over points and unless otherwise stated densities are at 20°/20° and indexes of refraction at 20°.

3-Methyl-1-Butene.—B. p., 21°; *d*, 0.660; *n* not given; mol. wt., 70. Purified by fractional distillation: b. p., 19–20°; d^{15}_{20}, 0.645; n^{18}, 1.3897; mol. wt., 66.8; double bond, 1.35. Although the material obtained was impure, there can be no doubt that the major part of it was 3-methyl-1-butene. It probably contained a low-boiling diene as impurity.

Table I

Compounds, Identification and Quantities

Compounds	Degree of identification	% in distillate	
		Straight	With Mg
C—C(C)—C=C	Positive	0.04	0.2
C=C(C)—C—C	Positive	.04	.2
C=C(C)—C=C	Positive	10.0	10.0
C—C(C)=C—C	Positive	.04	.2
C—C(C)=C—C—C Δ?	Chain structure positive	.06	.30
C—C—C(C)=C—C	Positive	.03	.15
C=C—C(C)=C—C	Positive except for position of double bonds	.03	.15
Benzene	Positive	.005	.1
C—C—C(C)=C—C—C	Chain structure positive	.03	.15
Δ^3—C—C_6H_9	Not positive	.01	.1
Δ^2—C—C_6H_9	Suspected	..	..
C—C=C—C—C—C(C)—C Δ?	Chain structure positive	.02	.1
Δ^1—C—C_6H_9	Positive	.1	1.0
Toluene	Positive	.05	1.0
C—C—C—C—C—C(C)=C Δ?	Chain structure positive	.04	.2
Dihydro-*m*-xylene	Positive	.1	1.0
m-Xylene	Positive	.05	1.0
 Δ?	Positive	.08	.8
 ?	Hydrogenation product  ?	.04	.8
p-Methylethylbenzene	Positive	.04	.8
$C_{10}H_{18}$ (1 double bond)	....	.04	.8
C—C(C)=C—C—C—C(C)=C—C Δ?	Not positive	.015	0.0
	Positive	20.0	20.0

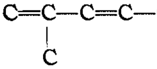
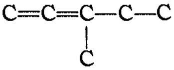
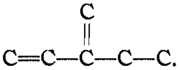
2-Methyl-1-Butene.—B. p., 32°; d_0^0, 0.667; n^{17}, 1.378. Purified by polymerization of the contained isoprene with sodium–potassium alloy, removal of the polymerized product, reduction of the remaining isoprene by sodium in liquid ammonia and subsequent fractional distillation: b. p. 30–31°; d_{20}^{17}, 0.6645; n^{17}, 1.3752; double bond, 1.0.

Isoprene.—B. p., 34°; *d*, 0.679; *n*, 1.4221. Purified by fractional distillation, identified by polymerization to synthetic rubber: b. p., 33–34°; *d*, 0.671; *n*, 1.4103. Bromination indicates 1.82 double bonds per C_5H_8. Pentenes were present as impurities.

2-Methyl-2-Butene.—B. p., 38.4°; d^{13}, 0.668. Purified by fractional distillation: b. p., 36.8–38°; *d*, 0.666; *n*, 1.3927; double bonds, 1.25 per C_5H_{10}. Isoprene present as impurity.

Component 59–60°.—*d*, 0.730; *n*, 1.4117; 1.0 double bond per C_6H_{12}. Purified by fractional distillation. Hydrogenation and nitration gave a material, b. p., 60–61°; *d*, 0.654; *n*, 1.3728; mol. wt., 87. I. C. T. gives for 2-methylpentane: b. p., 60°; *d*, 0.654, *n*, 1.372; mol. wt., 86. These results identify the original material as a 2-methylpentene, position of the double bond unknown.

3-Methyl-2-pentene.—Isomer No. 1: b. p., 65.7°; d^{15}, 0.722; *n*, 1.4065. Isomer No. 2: b. p., 70.2°; *d*, 0.698; *n*, 1.401. Purified by fractional distillation: b. p., 62–65°; *d*, 0.694; *n*, 1.404; double bond, 1.07 per C_6H_{12}. Hydrogenation gave a compound b. p., 63.6–64.5°; *d*, 0.666; *n*, 1.3752; mol. wt., 86. I. C. T. gives for 3-methylpentane: b. p., 64°; *d*, 0.668, *n*, 1.377, mol. wt., 86.

Component 76–79°.—Purified by aniline fractionation: *d*, 0.742; *n*, 1.4346; double bonds, 1.58 per C_6H_{10}. Partially hydrogenated, then extracted with H_2SO_4; adding water to the acid liberates an oil which gave on redistillation: b. p. 67–68°; *d*, 0.712; *n*, 1.4060; mol. wt., 83. Bromine reacted slowly. I. C. T. gives for 3-methyl-2-pentene two isomeric forms of which the average is: b. p., 67.8°; *d*, 0.712; *n*, 1.4039; mol. wt., 84. The following deductions may be made: 1.58 double bonds shows the presence of a diene in the original material; the partial hydrogenation and the extraction show that the carbon structure of this diene corresponds to 3-methyl-pentadiene. The forms compatible with the experimental results are:  $C{=}C(C){-}C{=}C{-}C$,  $C{=}C{=}C(C){-}C{-}C$ and  $C{=}C{-}C({=}C){-}C{-}C$. The only diene given in the literature boiling at 76–79° is 3-methyl-1,3-pentadiene, for which the constants by Abelmann are: b. p., 76–79°; d_4^0, 0.7576, $n^{16.5}$, 1.45427. A mixture of 64% of this diene, 31% of 3-methyl-2-pentene and 5% benzene will yield physical constants in close agreement with those of the original mixture. 3-Methyl-2-pentene and benzene are the adjoining and identified components. The identification is not considered as positive, despite the strong evidence.

Benzene.—M. p., 5.6°; b. p., 79.6°; *d*, 0.878; *n*, 1.5014.—Purified by aniline fractionation followed by a treatment with bromine and distillation: 2 cc. of purified material was obtained; m. p., +2°; *n*, 1.4995; characteristic odor of benzene.

Component 93–95°.—Purified by fractional distillation: *d*, 0.744, *n*, 1.422; 1.06 double bond per C_7H_{14}. Hydrogenation and nitration gave a compound: b. p., 92–95°; *d*, 0.723; *n*, 1.4032, which contained hexahydrotoluene as an impurity. The physical constants are not in sufficient agreement with anything in the literature to allow a possible identification. The nearest physical constants given are for *d*-3-methylhexane: b. p., 92°; *d*, 0.687. The physical constants of the hydrogenated product show that it contained a large proportion of a paraffinic hexane, the boiling point of which corresponds to the one given for 3-methylhexane. Identification considered incomplete.

Δ^3-Tetrahydrotoluene.—B. p., 103°; *d*, 0.799; *n*, 1.443. Purified by fractional distillation: b. p., 102–103°; *d*, 0.791; *n*, 1.444; double bond, 1.08 per C_7H_{12}. Hydrogenation gave a compound, b. p., 100–102°; *d*, 0.7671; *n*, 1.4225. I. C. T. gives for methylcyclohexane: b. p., 100.8°; *d*, 0.764; *n*, 1.4235. Nitration failed to detect aromatic compounds.

Δ^2-Tetrahydrotoluene.—Not purified enough for identification; a sufficient intermediate persisted in the general distillation to suggest its presence.

Component 109–110°.—Purified by aniline fractionation: *d*, 0.783; *n*, 1.4413; double bond, 1.13 per C_7H_{14}. Hydrogenation and nitration indicated toluene as an impurity. Further purification of the saturated compound by fractional distillation gave a small quantity of hexahydrotoluene and of *iso*-octane: b. p., 116°; *d*, 0.706; *n*, 1.397. I. C. T. gives for *iso*-octane: b. p., 116°; d_4^{15}, 0.704; *n*, 1.3964.

Δ^1-Tetrahydrotoluene.—B. p., 111°; *d*, 0.809; *n*, 1.4496. Purified by fractional distillation: b. p., 110–111°, *d*, 0.818; *n*, 1.4653. Special test (Beilstein): 3 drops of sulfuric acid added to an alcoholic solution of the hydrocarbon gave a green color peculiar to Δ^1-tetrahydrotoluene. Double bonds, 0.75, indicating a large percentage of toluene. Hydrogenation and nitration yielded a large quantity of trinitrotoluene and hexahydrotoluene: b. p., 100°; *d*, 0.762; *n*, 1.423. I. C. T. gives for hexahydrotoluene: b. p., 100.8°; *d*, 0.764; *n*, 1.4235.

Toluene.—B. p., 110.5°; *d*, 0.866; *n*, 1.4962. Purified by aniline fractionation, treatment with bromine and steam distillation: b. p., 110° sharp; identified by its odor and nitration to mononitrotoluene, b. p., 220°, the latter also having a characteristic odor.

Component 121–122°.—*d*, 0.765; *n*, 1.4287; hydrogenation and nitration indicated the presence of a small amount of aromatic compounds and gave a material: b. p., 116–121°; *d*, 0.739; *n*, 1.4102; mol. wt., 112.4, indicating *iso*-octane with a small quantity of hexahydro-*m*-xylene as an impurity. A fraction 124–125° gave a hydrogenation product with a slightly higher boiling range, density and index of refraction, indicating another isomeric form of 2-methylheptene containing an increased quantity of hexahydro-*m*-xylene. Although the above two fractions were present in the distillation in sufficient quantity to indicate the presence of components, there was not enough for proper purification and identification; all indications were that they were isomeric methylheptenes, probably 2-methylheptenes, with the location of the double bond totally unknown.

Dihydro-*m*-xylene, Probably Δ-1,3.—No constants given in the literature. Purified by aniline fractionation: b. p., 129–130°; *d*, 0.795; *n*, 1.4451. Hydrogenation and nitration indicated the presence of a small quantity of xylene and of a compound, b. p., 122–129°, bulk at 125°; *d*, 0.764; *n*, 1.4208; mol. wt., 112.6. I. C. T. gives for hexahydro-*m*-xylene: b. p., 123.7°; *d*, 0.771; *n*, 1.425; mol. wt., 112. These properties identify hexahydro-*m*-xylene with a small amount of paraffinic compounds as impurity. A substantial part of the original cut obtained by fractional distillation containing the dihydro-*m*-xylene was treated with bromine; no dibromides were found, only tetrabromides.

***m*-Xylene.**—B. p., 139°; *d*, 0.865; *n*, 1.4973.—Purified by treating with an excess of bromine water, and steam distilling; redistilling several times to eliminate all traces of bromides gave a material, b. p., 137°; *d*, 0.866. Nitration to the trinitro compound gave white crystals melting sharply at 179.5°. Mulliken gives m. p. 180–181° for trinitro-*m*-xylene. It is thus shown that the xylene obtained was pure *m*-xylene containing no trace of either ortho or para derivatives.

***p*-Tetrahydro-Ethyltoluene.**—Beilstein gives for the Δ^3-compound: b. p., 149°; *d*, 0.816; n^{16}, 1.453. Purified by fractional distillation: b. p., 144–145°; *d*, 0.813; *n*, 1.4529; double bond, 1.2 per C_9H_{16}. Hydrogenation and nitration gave a material: b. p., 147°; *d*, 0.784; *n*, 1.4335; mol. wt., 123. Beilstein gives for *p*-hexahydro-ethyltoluene: b. p., 147°; d_4^{15}, 0.788; n^{15}, 1.435; mol. wt., 126. There can be no question of the identification except for the position of the double bond, which may have been Δ^1 instead of Δ^3; no physical constants are available for the Δ^1-compound.

Component 158–159°.—*d*, 0.834; *n*, 1.4665; double bond, 0.998. Purified by fractional distillation; composition by combustion, $C_{10}H_{16}$, establishing the presence of a dicyclic compound. I. C. T. gives for thujene: b. p., 151°; *d*, 0.830; *n*, 1.4515. Hydrogenation and nitration gave a material, b. p., 158–161°; *d*, 0.813; *n*, 1.4498; mol. wt., 133.5–134.8 (theoretical for $C_{10}H_{18}$, 138); double bond, 0. Combustion gave $C_{10}H_{18}$ within 0.2%. Beilstein gives for thujane: b. p., 157°; *d*, 0.814–0.819; *n*, 1.4376–1.44395. Off-hand it would appear that the identification of the original material, as an isomeric form of thujene, was as definite as many of the foregoing identifications, but more careful consideration indicates that such is not the case. Identification by physical constants requires not only that the physical constants of the unknown be in close agreement with those of likely possibility, but that all, or nearly all, of the possibilities be known and listed, and that the constants are not in agreement with any of the other possibilities. This has been the case with all the components positively identified in C_5, C_6, C_7, C_8 and C_9, but it is not so with the dicyclic compound in C_{10}. It was therefore decided to consider the identification of this component as unestablished.

***p*-Ethyltoluene.**—B. p., 162; *d*, 0.862; *n*, 1.4943. Purified by treating with bromine water and steam distilling: b. p., 160.5–163°; *d*, 0.866; *n*, 1.4832; mol. wt., 120.4, instead of 120, theoretical; saturated toward bromine; oxidation with permanganate yields terephthalic acid.

Component 162–163°.—*d*, 0.828; *n*, 1.46; mol. wt. 130.5; bromination indicated 1.0 double bond. Obtained only from rubber decomposed in the presence of magnesium. Hydrogenation and nitration gave a compound b. p., 162–164°; *d*, 0.794; *n*, 1.4407; saturated toward bromine; mol. wt., 135; combustion indicated a formula of $C_{10}H_{20}$ within 0.2%. This shows that the original material was of empirical formula $C_{10}H_{18}$. The hydrogenation was a quantitative check on the original bromination. It is evident that this is a single ring compound containing 1 double bond. It is impossible to identify this compound from any known data.

Component 162–163°.—The distillate from rubber alone gave a component in this boiling range: *d*, 0.8105; *n*, 1.456; double bond, 1.4. Aniline fractionation failed to purify it further. Thus it is seen that the distillation of rubber alone gives a lighter material than the distillation with magnesium and that the unsaturation is 1.4 instead of 1.0 double bond, indicating the presence of a dienic compound. If this density be extrapolated to 100% diene, 0.783 is obtained. By a separate synthesis,[7] a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes was obtained, the physical constants of which were: b. p., 163–164°; *d*, 0.773. Considered as not a positive identification, but as strong evidence that a dimethyloctadiene was present.

Dipentene.—B. p., 176°; d^{18}, 0.865; *n*, 1.471. The density given by I. C. T. is apparently an error; Schimmel and Company give 0.844; Brühl gives $d_4^{20.85}$, 0.8402; Staudinger, d^{20}, 0.841. Purified by fractional distillation: b. p., 176°; *d*, 0.8435; *n*, 1.4712; double bonds, 1.96. Hydrogenation gave *p*-menthane: b. p., 170–171.2°; *d*, 0.796; *n*, 1.4387. I. C. T. gives for *p*-menthane: b. p., 170°; *d*, 0.793; *n*, 1.437. No evidence was obtained of the presence of myrcene, or a terpene, b. p., 168–169°, or of dimethylbutadiene.[4]

Derivation of the Structural Formula of the Products from That of Rubber.—Prior to entering upon this investigation, a method had been developed for illustrating the mechanism by which isoprene and dipentene form during destructive distillation. After the above results were ob-

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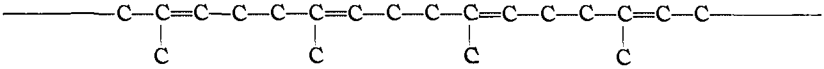
[7] Midgley and Henne, THIS JOURNAL, 51, 1294 (1929).

tained, it was felt that the method should be extended to include as many of the products as possible. A relatively simple solution is herewith presented which completely covers a majority of the cases, a few partially, and leaves only the formation of benzene without explanation. The long-chain structural formula for rubber hydrocarbon[8] is broken at single valences to give a section containing a given number of carbon atoms. The points of breakage are represented by partial valences and the double bonds are resolved into partial valence form. This is called the *transient form*. The following postulates are then observed: (1) adjacent partial valences may join to form double bonds (Thiele); (2) single partial valences six carbons apart may join to form rings; (3) any pair of partial valences may accept hydrogen, preferably those not adjacent to others; (4) partially hydrogenated aromatic compounds liberate hydrogen to yield the corresponding aromatic compounds; (5) partial valences not joining nor accepting hydrogen may migrate.

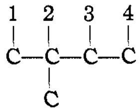


$$-\!-\!-\!-C-\underset{\substack{|\\ C}}{C}=C-C-C-\underset{\substack{|\\ C}}{C}=C-C-C-\underset{\substack{|\\ C}}{C}=C-C-C-\underset{\substack{|\\ C}}{C}=C-C-\!-\!-\!-$$

Staudinger formula for rubber

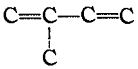
After having derived all of the combinations by applying the above assumptions to a transient form, the resulting *stable* forms are examined and those forms cast out which experimental data show do not form by pyrolytic decomposition. Predominant among these are molecules containing a carbon atom in a ring bonded to two other carbon atoms external from the ring and those containing a methylene group attached to a ring. The formation of dienic compounds has been disregarded, since no experimental data were obtained.

The mechanism of the reactions involving 5 carbon atoms (called compounds in C_5 for simplicity) may be represented as follows



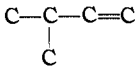
$$\overset{\substack{1\\ |}}{C}-\underset{\substack{|\\ C}}{\overset{\substack{2\\ |}}{C}}-\overset{\substack{3\\ |}}{C}-\overset{\substack{4\\ |}}{C}$$

Transient form in C_5



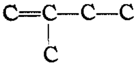
$$C=\underset{\substack{|\\ C}}{C}-C=C$$

Isoprene



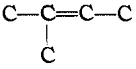
$$C-\underset{\substack{|\\ C}}{C}-C=C$$

3-Methyl-1-butene



$$C=\underset{\substack{|\\ C}}{C}-C-C$$

2-Methyl-1-butene



$$C-\underset{\substack{|\\ C}}{C}=C-C$$

2-Methyl-2-butene

Because of the preponderance of isoprene(C_5), dipentene(C_{10}) and heveen(C_{15}) in the products of destructive distillation, it is held certain that the single bond furthest removed from the double bonds is the most easily broken by pyrolysis. The same conclusion is arrived at by C. D.

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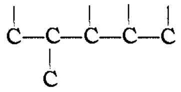
[8] Staudinger, *Ber.*, **44**, 2212 (1911); **46**, 2466 (1913); *Helv. Chim. Acta*, **5**, 743 (1922); **5**, 756 (1922); **5**, 785 (1922); *Ber.*, **57**, 1203 (1924); *Helv. Chim. Acta*, **7**, 842 (1924); *Z. angew. Chem.*, **38**, 226 (1925).

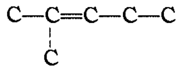
Hurd, starting from purely theoretical considerations,[9] and is found to hold when the other pyrolysis products of rubber are examined. Hence the transient form shown above predominates in C_5 to the practical exclusion of the two other possible forms. Four stable forms are derived from it: isoprene by the joining of 1 with 2 and 3 with 4, 3-methyl-1-butene by the acceptance of hydrogen on 1 and 2 and the joining of 3 with 4 and 2-methyl-1-butene by the acceptance of hydrogen on 1 and 4 and the joining of 2 with 3. Isoprene predominates, since it requires no hydrogen to produce a stable form.

In C_6, two transient forms are possible. Each case requires that a bond adjacent to a double bond be broken. The proportion of C_6 compounds should therefore be small. In neither case does a stable form result without either migration or hydrogen acceptance.



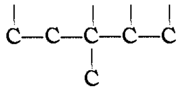
$\overset{|}{C}{-}\underset{\substack{|\\ C}}{C}{-}\overset{|}{C}{-}\overset{|}{C}{-}\overset{|}{C}$

Transient form No. 1 in C_6



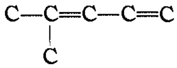
$C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}C$

2-Methyl-2-pentene



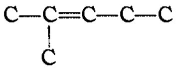
$\overset{|}{C}{-}C{-}\underset{\substack{|\\ C}}{\overset{|}{C}}{-}\overset{|}{C}{-}\overset{|}{C}$

Transient form
No. 2 in C_6



$C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{=}C$

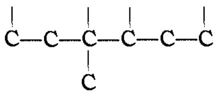
3-Methyl-1,3-pentadiene



$C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}C$

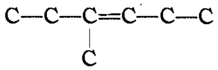
3-Methyl-2-pentene

There is only one transient form possible in C_7. It requires the breaking of two single bonds adjacent to double bonds. It is obvious that valences 1 and 6 may either accept hydrogen to form 3-methyl-3-hexene or join to form Δ^1-tetrahydrotoluene, the dehydrogenation of which gives toluene.



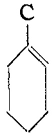
$\overset{|}{C}{-}C{-}\underset{\substack{|\\ C}}{\overset{|}{C}}{-}\overset{|}{C}{-}C{-}\overset{|}{C}$

Transient
form in C_7

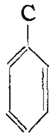


$C{-}C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}C$

3-Methyl-3-hexene

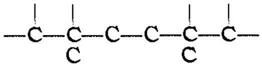


Δ^1-Tetrahydro-
toluene



Toluene

C_8 exhibits the possibility of only one transient form and in a similar manner to C_7 partial valences 1 and 6 may either hydrogenate to form a dienic compound or join to form dihydro-*m*-xylene, the dehydrogenation of which gives *m*-xylene.



${-}\overset{|}{C}{-}\underset{C}{\overset{|}{C}}{-}C{-}C{-}\underset{C}{\overset{|}{C}}{-}\overset{|}{C}{-}$

Transient
form in C_8

Dihydro-*m*-
xylene

m-Xylene

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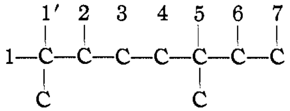
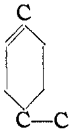
[9] C. D. Hurd, "The Pyrolysis of Carbon Compounds," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1929.

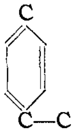
C_9 again presents two possible transient forms. The only evidence obtained covering the many possibilities in C_9 was in connection with transient form 1, which appeared to accept hydrogen by 1 and 1′, 2 joining with 7 and 5 with 6. The dehydrogenation of the resulting tetrahydro-*p*-ethyltoluene yields *p*-ethyltoluene. Other ring forms suggested as possible products of transient form 1 or 2 could not be detected.



Transient form
No. 1 in C_9

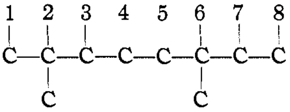


Tetrahydro-*p*-
ethyltoluene

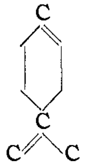


p-Ethyltoluene

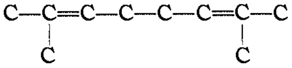
In C_{10}, as in C_5, three transient forms are possible, but since one of them is obtained by the rupture of only weak bonds, it should be predominant; it stabilizes without migration or hydrogenation by the joining of 3 with 8, 1 with 2 and 6 with 7, giving dipentene. By accepting hydrogen in 1,8 it stabilizes to dimethyloctadiene.



Predominating
transient form in C_{10}



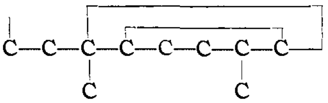
Dipentene



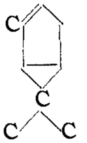
$\mathrm{C{-}\underset{\underset{\displaystyle C}{|}}{C}{=}C{-}C{-}C{-}C{=}\underset{\underset{\displaystyle C}{|}}{C}{-}C}$

Dimethyloctadiene

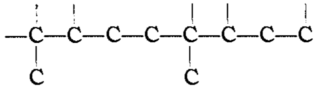
The other transient forms present an interesting speculation in connection with the component 158–159° (shown to be a dicyclic compound



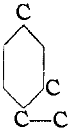
Transient form
No. 2 in C_{10}



Isomeric
thujene



Transient form
No. 3 in C_{10}



Component
162°?

$C_{10}H_{16}$), and component 162–163° (shown to be a single ring compound $C_{10}H_{18}$). The development from transient form 2 serves as a suggestion of the mechanism of the formation of a dicyclic compound, while the development from transient form 3 is a suggestion, predicated on the behavior of form 1 in C_9, to show the acceptance of hydrogen and subsequent ring formation. Both derivations are only speculations. If these suggestions could be proved experimentally, an interesting generality might be derived, namely, that when a terminal carbon atom has two partial valences attached to it, dicyclic ring formation is favored, but when an internal carbon is in the same case, hydrogen acceptance is favored.

The identification of Δ^3-tetrahydrotoluene and the evidence for the existence of Δ^2-tetrahydrotoluene among the products is not predictable. It is felt, however, that migration of the double bond from the Δ^1-position should not be considered as unlikely, since the amounts of Δ^2- and Δ^3-compounds were exceedingly small.

Discussion

In view of the evidence at hand, it can scarcely be doubted that with the exception of benzene the compounds of the aromatic series present were all derived by dehydrogenation of the corresponding hydro-aromatic forms, since only those aromatic compounds are found whose hydro-derivatives are also present. Dihydro-*m*-xylene is the only predictable ring compound in C_8, hence if dehydrogenation occurs, only *m*-xylene should result. If, on the other hand, *m*-xylene is a primary pyrolysis product, small amounts of the ortho and para derivatives at least should be present. Particular care was taken to ascertain that no other xylene was present than the meta derivative. The same reasoning holds true in C_9 with respect to *p*-ethyltoluene. A reason for the dehydrogenation during destructive distillation is not apparent. It is well known that cyclohexane in the presence of nickel and at similar temperatures will dehydrogenate to benzene, but there was no catalyst present to account for a similar behavior during pyrolysis of rubber alone. It is significant that the presence of magnesium in the rubber increases decidedly the proportion of aromatic compounds.

The origin of benzene is obscure. It is not due to accidental contamination in the laboratory, since the presence of a metal in the rubber always increases the amount of benzene in the distillate. Extreme pyrolysis in locally overheated spots might account for its formation.

To sum up, of the 23 compounds identified, 12 were in perfect agreement with the postulated results, 5 were in agreement as far as their identification was possible and rational explanations of the other 6 are not at variance with the postulates. In C_5 all forms predicted were obtained, in C_6, C_7 and C_8 chain compounds only were missing from the predictions. In C_9 the only logical rings were obtained, in fact, and in C_{10} all normal predictions were fulfilled.

Relationship of the Results to the Structural Formula of Rubber.—The constitution of the ten-carbon section of rubber has been thoroughly established by oxidation and confirmed by many investigators, but assemblage of these units into the complete structural formula of rubber has been the basis of much work and argument. Harries originally interpreted the results of his oxidations as indicating the existence of an eight-sided ring. He was more or less driven from his original interpretation in later years. Staudinger and co-workers[4,8] support a long-chain structure in which the ten carbon atom sections recur and are bonded together by ordinary valences, thus requiring no residual valences to account for the structure. Many intermediate speculations have been indulged in.

The results of this investigation throw no additional light upon the discussion. The use of the long-chain formula affords greater ease for interpretation, but the results do not contradict Harries viewpoint. Recently, E. A. Hauser[10] has supported the hypothesis that the rubber molecule is a long chain arranged in helix form, by interpreting the x-ray pattern of stretched rubber. The predominant formation of six-sided rings in C_7, C_8, C_9 and C_{10} appears to support this hypothesis, since to account for ring formation upon any other arrangement that has been advanced requires the joining of partial valences across the space occupied by six carbon atoms, whereas a helix may be so arranged that the carbon atoms, six apart in the chain, may be adjacent in space.

Conclusions

All of the products of the destructive distillation of natural rubber are directly derived, by simple reactions, from the rubber molecule. Those compounds predominate which represent sections of the rubber molecule occurring between the single bonds furthest removed from the double bonds.

Summary

Two hundred pounds of pale crepe rubber have been destructively distilled at atmospheric pressure. The distillate was fractionated and its components identified from C_5 to C_{10}, as shown in the table. Assuming that the Staudinger formula is correct, that the single bonds furthest from the double bonds are the weaker spots and that the formation of six-carbon rings is favored, it has been shown that nearly all of the compounds actually isolated could be predicted. The experimental results, together with forthcoming experimental data, are expected to be used to throw light upon the formula of the rubber molecule.

ITHACA, N. Y.

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[10] E. A. Hauser, address at the Swampscott Meeting of the American Chemical Society, September, 1928.