

amino-4-chlorothiophenol hydrochloride was dissolved in pyridine and one mole of the aldehyde or ketone was added dropwise to the warm solution. The mixture was finally heated on the water-bath. A few minutes to a half hour of heating sufficed for the aldehydes; the ketones required from one to six hours. The condensation product was precipitated by acidifying the cold solution.

Summary

1. Aliphatic aldehydes condense with 2-amino-4-chlorothiophenol to give benzothiazolines; aromatic aldehydes may give a benzothiazoline or a benzothiazole, depending upon the aldehyde employed.
2. Certain ketones condense with 2-amino-4-chlorothiophenol to give benzothiazolines.

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**NATURAL AND SYNTHETIC RUBBER. VIII. PRODUCTS OF THE
DESTRUCTIVE DISTILLATION OF SODIUM RUBBER**

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In the first paper¹ of this series it was shown that the pyrolysis products of natural rubber are directly related to the rubber molecule. The pyrolysis products of sodium rubber should bear a similar relationship to its molecular structure, and the difference between its formula and that of natural rubber should be detected by a study of these products.

Four kilograms of sodium rubber was destructively distilled. The resulting hydrocarbons were separated by fractional distillation, and identified by the methods previously employed.¹ The results are summarized in Table I. The starred compounds were identified by methods described in the experimental part. The components marked "abridged" were noted during the course of the fractionation, but were not investigated more fully due to the limited amount of available material.

The sodium rubber used was benzene free. Hence the presence of benzene among the distillation products confirms the viewpoint of its origin as expressed in paper I.

m-Xylene is not the only xylene formed. This agrees with the expectations based on the structure of sodium rubber indicated in a previous paper.² Mass action considerations predict the ratio of ortho:meta:para-xylene as 5:10:5, but actually it is found to be <1:10:2. The reduction of the *o*-isomer can be explained by the assumption made in paper I that free valences on secondary or tertiary carbon atoms will accept hydro-

¹ Midgley and Henne, *THIS JOURNAL*, **51**, 1215-1226 (1929).

² Ref. 1, pp. 1294-1296.

TABLE I
 COMPOUNDS, IDENTIFICATIONS AND QUANTITIES

Compounds	Degree of identification	Percentage in distillate
Propylenes and butenes	Positive	0.3
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$	Positive	0.2
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$	Positive	2.0
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Positive	1.1
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_3$	Positive	4.2
Component boiling at 58°	Abridged	0.05
3-Methylpentenes	Positive	.4
Component boiling at 68°	Abridged	.1
*Benzene	Positive	.1
*Isomeric heptane	Positive	.03
Component boiling at 93-95°	Abridged	.1
Tetrahydrotoluene	Positive	.4
Toluene	Positive	.1
Component boiling at 121-122°	Abridged	.2
*Hexahydroxylene	Possibly present	.1
* <i>o</i> -Xylene	Uncertain	.006
* <i>m</i> -Xylene	Positive	.1
* <i>p</i> -Xylene	Positive	.02
Compounds with 9 carbon atoms	Similar to those from natural rubber but not investigated	.5
*Compounds with 10 carbon atoms	Similar to those from natural rubber but in too small an amount to separate properly	6.4
*Dipentene	Uncertain	0.1
Normal pentane, isopentane and dihydroxylene were absent.		

gen rather than form rings. This does not explain the decrease of the *p*-isomer. It may be assumed that during the polymerization of isoprene, a directive force causes the 1,4-type of linkage of isoprene units to be favored. The result is a molecule more nearly resembling the natural rubber molecule in methyl group spacing than would be expected.³

Discussion

The comparison of the foregoing table with the similar table in paper I of this series is of primary interest. The significant similarities and differences in the pyrolysis products may be summarized as follows.

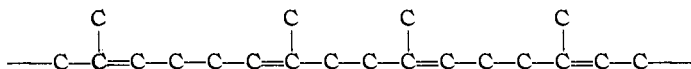
The arrangements of carbon atoms in the compounds obtained from natural and sodium rubber are the same, except for the position of some methyl groups. Compounds with five and ten carbon atoms predominate in both cases.

The products obtained from sodium rubber are more saturated. This is shown by the decrease of the quantities of isoprene and dipentene, the increase of the amount of pentenes, and the appearance of small amounts

³ Steimmig, *Ber.*, **47**, 350 (1914), has made a similar observation in his work on the ozonation of various synthetic rubbers.

of saturated hydrocarbons. The last were entirely absent in the natural rubber distillate.

These results together with the postulates of paper I confirm the carbon arrangement in the sodium rubber formula



but disagree with the conception of a recurring double bond. Bromine titration indicates one double bond per C_5H_8 unit. Ozonation gives an ozonide ($\text{C}_5\text{H}_8\text{O}_3$), but this ozonide does not break down on heating with water to give the simple compounds expected.⁴

Overvulcanized rubber behaves, in many respects, like sodium rubber. It still has one double bond for each sulfur-free C_5H_8 unit, as shown by the fact that these will accept two atoms of bromine, or one molecule of ozone. The ozonide is not severed into simple molecules by treatment with water. Pyrolysis yields little isoprene or dipentene, but considerable amounts of pentenes and decomposition products which are substantially the same as those obtained from sodium rubber.

Hence it may be concluded that the structural formula of sodium rubber is a modification of the one given above involving hydrogen migration or cyclization of such a nature that one chemically weak bond results for each C_5H_8 group and that this formula is a sulfur-free example of a rearrangement that occurs to some extent during the vulcanization of natural rubber.

Experimental Part

The sodium rubber used in this work was prepared by polymerizing boiling isoprene with liquid sodium-potassium alloy. The isoprene was prepared by the careful fractionation of the pyrolysis products of crepe rubber; it boiled at $31\text{--}35^\circ$, contained no benzene, and titration indicated 1.8 double bonds. The unpolymerized material was removed from the rubber by distilling from a steam-bath. The distillate consisted chiefly of 2-methyl-1-butene and 2-methyl-2-butene together with about 25% of unpolymerized isoprene.

A 3.86-kg. batch of this rubber which still contained the sodium-potassium alloy⁵ was then destructively distilled in the manner previously described.¹ A con-

⁴ Harries, *Ann.*, **383**, 217 (1911); **395**, 241 (1913); **406**, 180 (1914).

⁵ The presence of sodium-potassium alloy is not primarily responsible for the relatively low unsaturation of sodium rubber distillates. This is shown by the percentages of isoprene yielded in the fractions boiling from $32\text{--}38^\circ$ on pyrolysis of 100 g. batches of the following

Crepe rubber.....	65% isoprene
Crepe rubber + 6% Na-K.....	55% isoprene
Sodium rubber, alloy free.....	35% isoprene
Sodium rubber + 1% Na-K.....	18% isoprene

denser cooled with carbon dioxide snow was used to catch the more volatile materials. This condensate was warmed to room temperature and the escaping vapor passed into a solution of bromine in carbon tetrachloride. Fractional distillation yielded only 35 g. of propylene and butene dibromides boiling at 140–162° and having d_4^{20} 1.78.

The remainder of the hydrocarbons were separated and identified by the same methods as were previously employed, except as specifically mentioned hereafter. Due to the limited amount of material available, the complete identifications of certain minor constituents were omitted to make possible the investigation of other more important points. These cases are marked "abridged" in Table I.

Benzene.—The method of Rhodes, Gardner and Lewis⁶ was first employed to investigate the presence of benzene in a cut boiling at 76–80°. In ethylene bromide this cut showed a mean molecular weight of 87. In benzene, molecular weights of 107.5, 110 and 107 were found. The presence of 17.5% of benzene is thus indicated. The remainder of the cut was then brominated and steam distilled. After treatment with sulfuric acid, nitration gave dinitrobenzene, which was purified and identified by a mixed melting point determination with authentic material.

The formol reaction of Linke⁷ was used to establish the absence of any significant quantity of benzene in the isoprene from which the rubber was prepared. This reaction detects less than 0.1% of benzene in petroleum ether. A mixture of 25 cc. of isoprene and 2 cc. of pure *n*-heptane was saturated with bromine at 0° and the product steam distilled to bring over the heptane. The heptane was washed three times with concentrated sulfuric acid, and three drops of it were added to a mixture of 3 cc. of concentrated sulfuric acid and 2 drops of formaldehyde. No precipitate was formed. When the test was repeated with 0.02% benzene added to the isoprene, the characteristic precipitate was obtained in abundance.

Xylenes.—By bromination and steam distillation of several cuts boiling from 134–142°, a fraction rich in xylene was isolated. This fraction boiled at 136–142° and had d_4^{20} 0.827, n_D^{20} 1.4630 and a molecular weight in benzene of 112 and 112. The presence of a saturated hydrocarbon along with xylenes is thus indicated. A portion of this material was nitrated by the procedure of Mulliken⁸ and the crude mixture of nitro compounds was subjected to crystallization from alcohol; 77% of the nitro compound was recovered as trinitro-*m*-xylene, which was identified by a mixed melting point with authentic material.

Anal. Calcd. for $C_8H_7N_3O_6$: N, 17.42. Found: N, 17.29, 17.36.

From the mother liquors were obtained by recrystallization 14% of trinitro-*p*-xylene identified by a mixed melting point with authentic material.

An attempt was made to determine quantitatively the amounts of *o*- and *p*-xylenes present by a method similar to that used for benzene. The method was not quantitatively satisfactory due to the abnormal behavior of *o*- and *p*-xylenes as cryoscopic solvents. The results, however, did agree qualitatively with those obtained by the nitration method.

The oxidation of a small amount of the crude xylenes with potassium permanganate produced an acid which gave the fluorescein test for phthalic acid. This is evidence of the presence of *o*-xylene in small amount, estimated to be less than 0.006% of the original rubber.

Compounds with Ten Carbon Atoms.—More than 6% of the total distillate con-

⁶ Rhodes, Gardner and Lewis, *Ind. Eng. Chem.*, **20**, 85 (1928).

⁷ Linke, *Ber. deut. pharm. Ges.*, **11**, 258–262 (1901); *Chem. Centr.*, II, 130 (1920).

⁸ S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1904, Vol. I, p. 202.

sisted of compounds boiling from 158–176°. Prolonged fractionation failed to separate the components satisfactorily; fractionation from aniline was likewise of little value. Molecular weight determinations in benzene for the fractions in this range gave values from 133–139°. The two largest cuts in this range were examined more closely after aniline fractionation. The cuts boiled at 160–162.5° and 173–5.5° on Engler distillation and each comprised about 30% of the material boiling from 158–176°. The experimental data concerning these components are summarized below.

Component 160–162.5°: d_4^{20} 0.826; n_D^{20} 1.4627; mol. wt. in benzene 133, 133; double bonds 1.15. Combustion showed C, 87.44, 87.58; H, 12.14, 12.19, which is an empirical composition of $C_{10}H_{16.5}$. On hydrogenation 1.2 moles of hydrogen were absorbed. The resulting material boiled at 162–164°, and had d_4^{20} 0.791, n_D^{20} 1.4369, and mol. wt. in benzene 138, 139.

Component 173–175.5°: d_4^{20} 0.837; n_D^{20} 1.4709; mol. wt. in benzene 137, 136; double bonds 1.6. Combustion gave C, 87.61, 87.79; H, 12.15, 12.03, which is an empirical formula of $C_{10}H_{16.4}$. On hydrogenation 1.7 moles of hydrogen were absorbed; the product boiled at 170.5–172.5° and had d_4^{20} 0.804, n_D^{20} 1.4425 and mol. wt. in benzene of 139, 139. No dipentene tetrabromide could be obtained when the original hydrocarbon was brominated.

Saturated Compounds.—Various cuts were examined for saturated compounds by brominating, steam distilling, washing with sulfuric acid, redistilling and finally nitrating with mixed acid, washing with sulfuric acid and again redistilling. The observations are tabulated.

Boiling range, °C.	d_4^{20}	n_D^{20}	Mol. wt.	Percentage in total distillate	Remarks
ca. 75				0.003	Presence evident from low density and refractive index of benzene specimen.
92–93	0.726	1.4023		.03	Paraffin hydrocarbon present.
119–122	.765	1.4203	112, 112.5	.1	Naphthenic hydrocarbon present, presumably hexahydroxylene
136–142	.78 ^a		118 ^a	.1	Presumably a naphthenic hydrocarbon.

^a The properties of this material were extrapolated from those of the xylene fraction after determination of the amount of saturated hydrocarbon by the procedure of Spielman and Jones.⁹

Ozonation of Sodium Rubber and of Overcured Rubber.—The sodium rubber was purified before ozonation by the following procedure. A sample was dissolved in benzene, and alcohol was slowly added to react with the sodium–potassium alloy and to precipitate the rubber. The rubber was boiled out with water and then redissolved in benzene and reprecipitated with alcohol twice more. After removal of solvents in vacuum, a double bond determination by the method of Lewis and McAdams¹⁰ showed the presence of 1.0 double bond per C_5H_8 unit.

The overcured rubber was prepared by curing a rubber–sulfur mix for 150 hours at 150°. Analysis showed 5.7% combined sulfur and 0.11% free sulfur; a double bond determination indicated 0.84 double bond per C_5H_8 unit.

⁹ Spielman and Jones, *J. Soc. Chem. Ind.*, **36**, 489–490 (1917).

¹⁰ Lewis and McAdams, *Ind. Eng. Chem.*, **12**, 673 (1920).

Ozonation of the samples was carried out in carbon tetrachloride to which 5% of glacial acetic acid was added. Solvent loss was made up by adding more acetic acid. The sodium rubber was soluble in this mixture, while it was necessary to grind the overcured rubber finely and suspend it in the solution. Solvents were removed from the ozonides in high vacuum. On boiling the ozonides with water only traces of material of low molecular weight were obtained. In each case about half the ozonide was dissolved by the water and could be thus separated; the remainder formed a solid. Analyses of the ozonides and of various fractions separated by water are given in Table II. The sample of sodium rubber ozonide had turned very black during the removal of solvents in vacuum.

TABLE II
ANALYSES OF OZONIDES

	C, %		H, %		S, %		Empirical formula
Sodium rubber ozonide	54.65	55.05	7.29	7.43			$C_8H_8O_{2.6}$
Water-insoluble material from sodium rubber ozonide	65.37	65.47	7.55	7.45			$C_8H_{6.8}O_{1.55}$
Overcured rubber ozonide	53.39	53.30	6.44	6.46	4.57	4.45	$[(C_8H_8S)(C_8H_8O_2)_{0.14}]_n$
First water extract from overcured rubber ozonide	49.2		6.6		1.86	1.97
Second water extract from overcured rubber ozonide	52.64	52.55	6.23	6.43	4.66	4.80
Solid insoluble in water from overcured rubber ozonide	61.21	61.28	6.16	6.18	5.32	5.38

Summary

The pyrolysis products of sodium rubber have been compared with those of natural rubber. They indicate that sodium rubber is isomeric with natural rubber in the positioning of its methyl groups, and that the double bond of sodium rubber differs from the true ethylenic bond of natural rubber. In the latter respect sodium rubber closely resembles overvulcanized rubber.

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