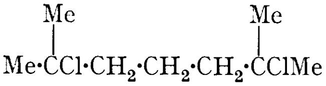
293. *The Action of Zinc Dust and Alcohol on the Hydrochlorides of Gutta-percha and Balata.*

By Thomas Hardie and John A. Mair.

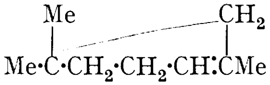
In 1921 Harries and Evers (*Wiss. Veröffent. Siemens-Konz.*, **1**, Heft 2, p. 87; *Chem. Zentr.*, 1921, **3**, 1358; *Chem. Abs.*, 1922, **16**, 3232) described a partial hydrogenation of caoutchouc by the action of zinc dust on an ethylene dichloride solution of the hydrochloride containing free hydrogen chloride. The product, a white solid of the formula $(C_{10}H_{18})_4$, and still unsaturated, was named α-hydrocaoutchouc. Staudinger and Widmer (*Helv. Chim. Acta*, 1926, **9**, 529), on repeating this work, found that, instead of a reduction, inner condensation or ring formation took place. With zinc dust alone, the product was a white substance about half as unsaturated as caoutchouc but still having the same empirical formula $(C_5H_8)_x$; this was named mono*cyclo*caoutchouc. With zinc dust and hydrochloric acid the product was similar in appearance and in composition, but had only one double bond to every 3 or 4 isoprene groups; it was termed poly*cyclo*caoutchouc. The same results were obtained with caoutchouc hydrobromide in place of the hydrochloride, whereas metals other than zinc, *e.g.*, iron and tin, gave similar but impure products, and aluminium-bronze and magnesium yielded products still rich in chlorine.

Staudinger and Widmer therefore examined the action of zinc dust and hydrochloric acid on mono- and di-chloro-paraffins and terpenes in which the chlorine was attached to the same carbon atom as a methyl group—corresponding to the probable structure of caoutchouc hydrochloride—and found that the chlorine was always split off as hydrogen chloride; *e.g.*, 2 : 6-dichloro-2 : 6-dimethylheptane (I) with zinc dust and hydrochloric acid gave α- and β-*cyclo*geraniolene, (II) and (III). From analogy with these results, the following structures for mono*cyclo*caoutchouc, etc., were proposed:

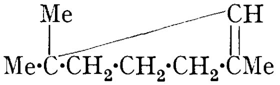


$\mathrm{Me{\cdot}\overset{\overset{Me}{|}}{C}Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\overset{Me}{|}}{C}ClMe}$

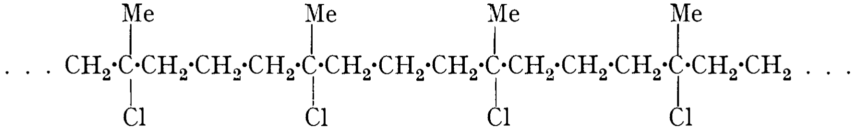
(I.)



(II.)

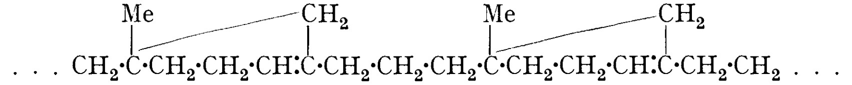


(III.)

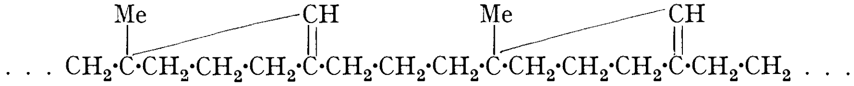


$$\ldots\ \mathrm{CH_2{\cdot}\underset{\underset{Cl}{|}}{\overset{\overset{Me}{|}}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{\underset{Cl}{|}}{\overset{\overset{Me}{|}}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{\underset{Cl}{|}}{\overset{\overset{Me}{|}}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{\underset{Cl}{|}}{\overset{\overset{Me}{|}}{C}}{\cdot}CH_2{\cdot}CH_2}\ \ldots$$

Caoutchouc hydrochloride.



α-Mono*cyclo*caoutchouc.



β-Mono*cyclo*caoutchouc.

These formulæ correspond with the possible formation of mono*cyclo*caoutchouc, but the mechanism of the further cyclisation to poly*cyclo*caoutchouc is not known.

Mono*cyclo*caoutchouc is soluble in benzene and light petroleum, insoluble in alcohol, acetone, and ether; poly*cyclo*caoutchouc is soluble in benzene and chloroform, partly soluble in ether, and insoluble in acetone and alcohol. The substances can be hydrogenated at high temperatures and pressures; and ozone and potassium permanganate give oxides $(C_5H_8O)_x$, in which the newly formed cycles have apparently been broken. *cyclo*Caoutchouc (*d* 0·992) is denser than caoutchouc (*d* 0·920), thus supporting the assumption of cyclisation, and its heat of combustion is lower, showing that the cyclisation is exothermic.

Staudinger and Geiger (*Helv. Chim. Acta*, 1926, **9**, 549) also found that when caoutchouc was heated in a vacuum, cyclisation began at about 200° and was rapid above 270°. The product was a poly*cyclo*caoutchouc having only one double bond to every five isoprene groups; it was a pale brown powder of empirical formula $(C_5H_8)_x$, *M ca.* 2200, and *d* 0·992. Poly*cyclo*gutta-percha was obtained by the same method (Geiger, *Annalen*, 1929, **468**, 47) as a white powder soluble in ether, but otherwise having similar solubilities to poly*cyclo*caoutchouc; and a like product was obtained by the action of zinc dust and hydrochloric acid on gutta-percha hydrochloride. *cyclo*-Caoutchouc and -gutta-percha have also been prepared (Staudinger and Bondy, *ibid.*, p. 1) by heating solutions of the ordinary substances to high temperatures.

Caoutchouc has also been cyclised by heating it at 90° in hydrogen at 60 atm. in presence of platinum-black (Pummerer, Nielsen, and Gundel, *Ber.*, 1927, **60**, 2167), by simple heating in sealed tubes (Fisher and Gray, *Ind. Eng. Chem.*, 1926, **18**, 414), by the action of organic sulphonyl chlorides and acids (Fisher, *ibid.*, 1927, **19**, 1325), and by the action of sulphuric acid on its benzene solutions (Kirchof, *Kolloid-Z.*, 1922, **30**, 176). All these procedures give products which are less unsaturated than caoutchouc but have the same empirical formula. Bruson, Sebrell, and Calvert (*Ind. Eng. Chem.*, 1927, **19**, 1033) obtained a compound, $(C_5H_8)_{10},SnCl_4$, by the action of stannic chloride on benzene solutions of caoutchouc; this is decomposed by alcohol, with regeneration of its constituents, the hydrocarbon being precipitated as a white amorphous powder having the same composition as caoutchouc but being more saturated and having no elastic properties.

The present paper records attempts to reduce the hydrochlorides of gutta-percha and balata in ethylene dichloride solution by means of zinc dust and alcohol, since reduction products prepared by a method other than catalytic hydrogenation should be of some interest. The milder reducing agents were expected to avoid the cyclisation caused by zinc dust and hydrochloric acid and (as shown in preliminary experiments) by zinc dust alone.

The reaction proceeds smoothly and the products, isolated by precipitation with alcohol and careful desiccation from an ethereal solution, were white friable powders, still of the composition $(C_5H_8)_x$, but totally unlike the parent hydrocarbons in appearance; the unsaturation was approximately half that of the original hydrocarbon, so the products are mono*cyclo*-balata and -gutta-percha, analogous to Staudinger's compound. They are soluble in ether, chloroform, carbon tetrachloride, and benzene, slightly soluble in light petroleum, and insoluble in alcohol, acetone, and acetic acid; moreover, their increased density also indicated cyclisation.

The cyclised products did not depress the f. p. of benzene, but molecular-weight determinations in camphor (Rast) gave values of 2000—4000, depending on concentration. Although this method is unreliable for this type of substance, the decrease in molecular weight caused by the above treatment is in accord with the increased solubility and more mobile solutions of the products.

In each preparation a small proportion (usually 5—10%) of the yield was insoluble in ether; this fraction had the same composition $(C_5H_8)_x$ and approximately the same unsaturation, and is thus also a mono*cyclo*-product. The soluble and the insoluble substances may be termed respectively α- and β-*mono*cyclo*gutta-percha* and -*mono*cyclo*balata*, but this does not necessarily imply that they have the α- and β-structures suggested by Staudinger.

The α-mono*cyclo*-compounds did not distil appreciably at 360°/2—3 mm., thus indicating greater stability than that of the parent substances, but further cyclisation took place to give poly*cyclo*-compounds with an unsaturation about 25% of that of the original hydrocarbon. The mono*cyclo*-compounds could not be hydrogenated at ordinary temperatures and pressures, but their hydrochlorides and hydrobromides were prepared; these were very similar in appearance to the corresponding compounds of gutta-percha and balata, and still retained the cyclic structure, as shown by density measurements; the hydrobromides were somewhat unstable.

EXPERIMENTAL.

The hydrocarbons were purified by the usual method (J., 1932, 593). The hydrochlorides were prepared in 85% yield by saturating a solution of 10 g. of hydrocarbon in 300 c.c. of chloroform with dry hydrogen chloride, excess of which was removed by a current of air, and running the solution (which showed a marked decrease in viscosity) in a thin stream into a large volume of acetone with vigorous stirring. The hydrochloride separated in white powdery flakes. The zinc dust was washed with very dilute aqueous ammonia, dried, and kept in a desiccator.

α- *and* β-*Mono*cyclo*gutta-percha*.—20 G. of gutta-percha hydrochloride were dissolved in 400 c.c. of ethylene dichloride, 75 c.c. of absolute alcohol added, and then 10 g. of zinc dust. The mixture was heated under reflux in an atmosphere of carbon dioxide, with further small additions of zinc dust, till a sample showed no trace of chlorine (about 8 days). No evolution of hydrogen chloride took place. The mobile, pale yellow solution was filtered from zinc dust and zinc chloride, concentrated by distillation under reduced pressure at 40°, and run into a large volume of absolute alcohol at 0° with vigorous stirring; the sticky clot which separated was redissolved in ether, a small portion remaining insoluble. The ethereal solution on desiccation gave 11 g. of α-*mono*cyclo*gutta-percha* as a white friable solid [Found : C, 88·0, 87·9; H, 11·6, 11·7. $(C_5H_8)_x$ requires C, 88·2; H, 11·8%], totally unlike gutta-percha in appearance. The ether-insoluble portion, when dried, gave 0·5 g. of the β-*isomeride* as a faintly yellow amorphous powder (Found : C, 87·9, 87·9; H, 11·6, 11·6%).

To verify the occurrence of cyclisation, the unsaturation was determined by adding excess of 1% bromine solution in chloroform to a solution of the product in the same solvent, the temperature being kept at 0°, and determining the excess of bromine by addition of aqueous potassium iodide and back-titration with sodium thiosulphate. Subsequent addition of potassium iodate and titration with thiosulphate accounted for any bromine used in substitution (Found : in α-compound, unsaturation, 51·16, 51·42; in β-compound, unsaturation, 49·45, 49·71%). Both fractions, therefore, being approximately half as unsaturated as gutta-percha itself, are cyclic, and differ only in their solubility in ether. The ether-soluble fraction softens at 70° and melts to a clear brown liquid at 85—90° (decomp. 120°); the ether-insoluble fraction softens about 65—68°, melts at 84—86°, and decomposes at 120°.

α- *and* β-*Mono*cyclo*balata*.—Balata hydrochloride, similarly prepared and treated, gave similar products : ether-soluble fraction, m. p. 100—105° (decomp. 120—125°) (Found : C, 88·1, 88·0; H, 11·7, 11·7; unsaturation, 46·1, 47·7%); ether-insoluble fraction, an amorphous pale yellow powder, m. p. *ca.* 100° (softening at 85—90°; decomp. 115—120°) (Found : C, 88·0, 88·0; H, 11·7, 11·7; unsaturation, 48·0, 47·7%).

Densities, measured in absolute alcohol at 19°, were : Mono*cyclo*gutta-percha, 0·9965; gutta-percha, 0·920; mono*cyclo*balata, 1·0030; balata, 0·920. Molecular-weight determinations for concentrations of 2·5—20% in camphor gave : mono*cyclo*gutta-percha, α, 1550—4000; β, 1800—3640; mono*cyclo*balata, 2000—3723 and 1940—3300 for the two fractions.

Mono*cyclo*gutta-percha, when heated at 2—3 mm. pressure, melted and bubbled vigorously at 150°, and at 180° had set to a shiny, brown, porous mass, remaining unchanged even above 360°. The distillate was negligible, and the residue, amounting to 84% of the original material, showed an unsaturation of 25·03%. Mono*cyclo*balata behaved similarly, the residue having an unsaturation of 24·5%. 1·590 G. of mono*cyclo*gutta-percha, in 80 c.c. of benzene with 1 g. of active palladium as catalyst, were shaken with hydrogen at ordinary temperature and pressure for 100 hours; 106 c.c. were absorbed (calc., 262 c.c.). Mono*cyclo*balata also could not be completely hydrogenated.

The hydrochlorides and hydrobromides of mono*cyclo*-gutta-percha and -balata were prepared by the usual saturation method, and in the following table their densities are compared with those of the corresponding derivatives of the uncyclised hydrocarbons :

	Hydrochloride.	Hydrobromide.		Hydrochloride.	Hydrobromide.
Mono*cyclo*gutta-percha	1·040	1·070	Gutta-percha	0·961	0·980
Mono*cyclo*balata	1·055	1·071	Balata	0·9645	0·970

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THE UNIVERSITY, GLASGOW

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