# 294. *Condensation of Balata Bromide with Phenols and Phenolic Ethers.*

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The Friedel–Crafts reaction was first applied to caoutchouc bromide by Weber (*Ber.*, 1900, **33**, 791), who, by the condensation with phenol, obtained a compound which he represented as $[C_{10}H_{16}(O\cdot C_6H_5)_4]_x$. This "tetroxylphenylpolyprene" was soluble in alkalis and insoluble in benzene. Since anisole did not condense in this manner, Weber concluded that the hydroxyl group was the point of attack, and so described the compound as an ether. Fisher, Gray, and McColm (*J. Amer. Chem. Soc.*, 1926, **48**, 1309) repeated this reaction and found that the product could be methylated easily; since the methylated substance was soluble in benzene and insoluble in alkali, they deduced that the original product contains free hydroxyl groups, and assumed the reaction to involve the *p*-hydrogen atom of the phenol and to be

$$[\cdot CH_2\cdot CMeBr\cdot CHBr\cdot CH_2\cdot]_x + 2xC_6H_5\cdot OH \longrightarrow [\cdot CH_2\cdot CMe(C_6H_4\cdot OH)\cdot CH(C_6H_4\cdot OH)\cdot CH_2\cdot]_x + 2xHBr.$$

They named this substance "di(hydroxyphenyl)hydrorubber," and obtained it in nearly quantitative yield by using ferric chloride as condensing agent. The compounds gave no depression of the freezing point of benzene, and showed colloidal properties, so it was inferred that the parent hydrocarbon had very large colloidal molecules.

Geiger (*Helv. Chim. Acta*, 1927, **10**, 530) extended this work to a series of phenols and phenolic ethers and also to gutta-percha bromide, which reacted in an exactly similar manner. With phenolic ethers the reaction was slower than with phenols and the yields were poor. By condensing caoutchouc bromide with anisole, a compound was obtained in one step which was identical with Fisher, Gray, and McColm's methylation product; this substance (I; with OMe in place of OH) was termed dimethoxydiphenylhydrocaoutchouc. Geiger also prepared benzoates of the phenolic products by the Schotten–Baumann reaction, so confirming the presence of hydroxyl groups; and from gutta-percha bromide he obtained compounds similar to those from caoutchouc bromide but having lower melting points. He, too, assumed the *p*-hydrogen atom to react, by analogy with simpler compounds. No depression of the freezing point of benzene was observed with any of the compounds, and those examined by *X*-rays gave "amorphous" rings. Staudinger (*Kautschuk*, 1926, 103) states that such products as the above are much more complicated than is supposed, their formation involving not only condensation but cyclisation; this has not been substantiated, however.

The present work was undertaken with a view to extend these investigations to balata bromide. This substance, when newly prepared, reacts very readily with excess of phenolic compounds in presence of anhydrous ferric chloride at 100—120° with evolution of hydrogen bromide. The resulting compounds, purified by repeated solution and precipitation, are very soluble in alkalis, and readily give p-*nitrobenzoates*, showing the presence of hydroxyl groups. From a similar reaction at a slightly higher temperature with anisole and phenetole the yields were low, but the products were easily isolated by their solubility in acetone or ethyl acetate. Since the corresponding anisole and phenetole condensation products with gutta-percha bromide have not been described, these were also prepared.

Analysis of the phenol condensation product, *dihydroxydiphenylhydrobalata*, agrees very closely with the formula $[C_5H_8(C_6H_4\cdot OH)_2]_x$, and the other products have similar formulæ. That the *p*-hydrogen atom is involved has been proved by oxidation of dihydroxydiphenylhydrobalata by potassium permanganate in acetone solution, *p*-hydroxybenzoic acid being isolated.

All the condensation products are coloured, amorphous powders of somewhat indefinite m. p. They are mostly soluble in acetone, ethyl acetate, and pyridine, but insoluble in light petroleum, acids, and water; in addition, the phenolic products are soluble in alkalis and slightly soluble in benzene. None of them gives a depression of the freezing point of benzene, and molecular-weight determinations (Rast) give variable results (compare Staudinger, *Ber.*, 1928, **61**, 2575). The colloidal nature of the solutions indicates that the molecules are probably not much smaller than those of the hydrocarbon—this applies to the *p*-nitrobenzoates, which are the products of three successive reactions. Many of the condensation products give fluorescent solutions, and those of resorcinol with both gutta-percha and balata are good indicators in acidimetry and also behave as adsorption indicators in argentometric titrations.

The products from caoutchouc, gutta-percha, and balata are all similar in being coloured, amorphous substances of high molecular weight. The melting points of the derivatives of the last two substances are slightly lower than those of the first.

## EXPERIMENTAL.

The balata and gutta-percha were purified as described by Mair and Todd (J., 1932, 393), and the bromides were prepared as fine white powders in 90% yield by the method of Weber (" The Chemistry of India Rubber," p. 32).

p-*Dihydroxydiphenylhydrobalata*.—6·25 G. of balata bromide, 2·5 g. of anhydrous ferric chloride, and 20 g. of phenol were heated on an oil-bath at 100—120° for 2½ hours, hydrogen bromide being vigorously evolved. After cooling, the thick liquid was diluted with 50 c.c. of alcohol, and the solution poured into 500 c.c. of warm dilute hydrochloric acid. The dark brown precipitate was filtered off, and purified by repeated solution in acetone and precipitation with dilute acid. The final product was 5 g. of a chocolate-brown powder, m. p. 195—200° (shrinking at 130°) {Found : C, 79·8, 80·1; H, 7·4, 7·15. $[C_5H_8(C_6H_4\cdot OH)_2]_x$ requires C, 80·3; H, 7·1%}, whose ethyl acetate and benzene solutions were faintly fluorescent. The p-*nitrobenzoate*, prepared in the usual manner, is also a brown powder, m. p. 87—90° [Found : N, 5·2, 5·1. $(C_{31}H_{24}O_8N_2)_x$ requires N, 5·1%].

*Oxidation.* 20 G. of the compound were oxidised at room temperature in purified acetone solution with the theoretical quantity (80 g. = 13 atoms of oxygen) of finely ground potassium permanganate, dusted into the solution in small quantities with constant stirring. The solution was then evaporated to dryness, leached with hot water, and sulphur dioxide passed till the manganese dioxide dissolved. The resulting white flocculent precipitate was filtered off, and found to be partly soluble in hot water, the insoluble part consisting of complex resin acids. The aqueous solution was slowly evaporated, and the *p*-hydroxybenzoic acid which separated out was recrystallised from water; m. p. 211°; its acetyl derivative, prepared by Chattaway's method (J., 1931, 2495), melted at 186°.

*Dihydroxy*-p-*tolylhydrobalata*.—2 G. of balata bromide, 1 g. of anhydrous ferric chloride, and 10 g. of *p*-cresol were heated on an oil-bath at 100—120° for 2 hours. The cooled dark brown liquid was poured into 400 c.c. of 1% sodium hydroxide solution, the solid filtered off, and extracted at 80° with 150 c.c. of dilute hydrochloric acid to remove iron salts; it was then dissolved in acetone and poured into dilute hydrochloric, giving finally 1·5 g. of a greenish-grey powder, m. p. 167—169° {Found : C, 80·3, 80·4; H, 7·8, 7·8. $[C_5H_8(C_6H_3Me\cdot OH)_2]_x$ requires C, 80·8; H, 7·8%}, showing a colour change when its acid suspension is made alkaline. The p-*nitrobenzoate* was a light brown powder, m. p. 143—145° [Found : N, 4·9, 4·9. $(C_{33}H_{28}O_8N_2)_x$ requires N, 4·8%].

*m*-Cresol similarly afforded 2·1 g. of a green powder, m. p. 165—169° (shrinking at 140°) (*p*-nitrobenzoate, yellow, m. p. 146—148°); and *o*-cresol gave 1·8 g. of a brown compound, m. p. 193—195° (*p*-nitrobenzoate, brown, m. p. 190—192°).

*Tetrahydroxydiphenylhydrobalata*.—2·5 G. of balata bromide, 1·25 g. of anhydrous ferric chloride, and 12 g. of resorcinol were heated at 100—130° for 2½ hours, cooled, and digested with 150 c.c. of alcohol at 80° for an hour. The liquid was then poured into 500 c.c. of dilute hydrochloric acid, and the precipitated product on purification gave 2·9 g. of deep red *tetrahydroxydiphenylhydrobalata*, m. p. 220° [Found : C, 71·2, 70·9; H, 6·2, 6·4. $(C_{17}H_{18}O_4)_x$ requires C, 71·3; H, 6·3%]. The p-*nitrobenzoate* was reddish-violet, m. p. 195—200° [Found : N, 6·3, 6·4. $(C_{45}H_{30}O_{16}N_4)_x$ requires N, 6·35%].

*Indicator properties.* The alcoholic solution of tetrahydroxydiphenylhydrobalata showed strong green fluorescence, and in dilute solution possessed marked indicator properties. Since Geiger (*loc. cit.*) makes no mention of similar properties in the gutta-percha analogue, both this compound (dark orange powder, m. p. 270°) and the caoutchouc analogue were prepared and found to possess similar fluorescence and indicator properties. It is significant that only the resorcinol condensation products behave in this manner (cf. Weissberger and Thiele, J., 1934, 148).

When resorcinol is heated with ferric chloride to 110°, the product, after purification by solution in alcohol and precipitation with dilute hydrochloric acid, is a dark red, viscous solid, soluble in alkalis with an intense green fluorescence; its alcoholic solution or a dilute solution of its sodium salt shows indicator properties similar to, but less well-defined than, those of the three foregoing condensation products, the colour being less pure, with a permanent yellow tint. It seems probable, therefore, that the indicator properties of the latter compounds are really due to condensation products of resorcinol itself, their relative sharpness being attributable to selective adsorption of one constituent of the complex mixture formed by secondary reaction between the resorcinol and the anhydrous ferric chloride.

p-*Dimethoxydiphenylhydrobalata.*—1·6 G. of balata bromide, 1 g. of ferric chloride, and 6·6 g. of anisole were heated together as before (100—130°; 3 hrs.) and cooled; 100 c.c. of benzene were added, and the solution filtered into alcohol containing hydrochloric acid. The precipitate was purified by running its benzene solution into light petroleum. p-*Dimethoxydiphenylhydrobalata* was then obtained (2 g.) as a grey-brown powder, m. p. 105—110° [Found: C, 80·6, 80·7; H, 7·4, 7·6. $(C_{19}H_{22}O_2)_x$ requires C, 80·8; H, 7·8%]; its ethyl acetate solution was fluorescent, and the benzene solution weakly so.

p-*Diethoxydiphenylhydrobalata.*—This *substance*, prepared by using phenetole as above (yield 3 g.), was yellow-brown, m. p. 125—130°, with fluorescent properties [Found: C, 82·9, 81·5; H, 8·1, 8·3. $(C_{21}H_{26}O_2)_x$ requires C, 81·3; H, 8·4%].

By similar methods were obtained p-*dimethoxydiphenylhydrogutta-percha* (2 g.) as a greenish-brown product, m. p. 195—197° (Found: C, 80·4; H, 7·7%), and the *diethoxy*-compound (1·5 g.), greenish-brown, m. p. 205—207° (Found: C, 81·0; H, 8·3%), both giving fluorescent solutions in ethyl acetate.

α-*Dihydroxydinaphthylhydrobalata.*—3 G. of balata bromide, 2·5 g. of anhydrous ferric chloride, and 20 g. of α-naphthol were heated together for 3 hours at 100—105°, cooled, treated with 200 c.c. of absolute alcohol, and the precipitate collected, dissolved in acetone, and re-precipitated by pouring into dilute hydrochloric acid. Thus purified, the *substance* (3·2 g.) had a putty-grey colour, m. p. 190—195° [Found: C, 84·1, 84·3; H, 6·1, 6·1. $(C_{25}H_{22}O_2)_x$ requires C, 84·7; H, 6·2%]; p-*nitrobenzoate*, dark brown, m. p. 150—152° [Found: N, 4·2, 4·3. $(C_{39}H_{28}O_8N_2)_x$ requires N, 4·3%].

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