



very kindly carried out direct comparisons of his dehydropodophyllotoxin with our compound III. He reports that the two materials are the same.

Ketones IIa and IIb should prove of value in elaborating structural and stereochemical derivatives of podophyllotoxin.

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POLYTHIOLSTYRENE—A NEW OXIDATION-REDUCTION ION EXCHANGE RESIN

Sir:

Oxidation-reduction polymers of the dihydroxybenzene type have been described by Cassidy¹ and Manecke.² We wish to report on a new oxidation-reduction resin of the thiophenol type.

Polystyrene (mol. wt. 30,000) was nitrated³ to form polynitrostyrene, which was reduced by hydrogenation using a palladium catalyst to polyaminostyrene. Calcd. for C₈H₉N: N, 11.75. Found: N, 11.25.

Diazotization of polyaminostyrene with nitrous acid to form the diazonium chloride, followed by treatment with potassium ethylxanthate, gave insoluble polystyrene xanthate. Calcd. for C₁₁H₁₂OS₂: S, 28.58. Found: S, 26.96. Conversion to the polythiol was by hydrolysis with base, then acidification with acid to give polythiolstyrene. Calcd. for C₈H₈S: 23.50. Found: 21.77.

The resin was obtained as large brown granules; these were ground to a powder which was insoluble in all common solvents and swelled about 25% in alkaline solutions. Cross-linking probably occurred during decomposition of the diazo polymer.

(1) H. G. Cassidy, *et al.*, *THIS JOURNAL*, **75**, 1615 (1953).

(2) G. Manecke, *Z. Elektrochem. Ber. Bunsenges. physik. Chem.*, **58**, 369 (1954).

(3) A. Skogseid, *Dissertation*, Oslo, 1948.

The reducing capacity of the resin was determined in columns containing 0.1–0.4 g. of resin. Reductions were carried out using excess amounts of 0.5–2 *M* solutions of either sodium hydrosulfite, sodium sulfide or thioglycolic acid (at *pH* 8). The resin was then oxidized with known amounts of standard 0.1 *N* iodine in 0.25 *N* potassium iodide in a phosphate buffer (*pH* 8). The reducing capacity as calculated from back-titrations of the iodine effluent was 6.6 ± 0.4 meq./g. of resin for about ten consecutive cycles each on two columns. The theoretical capacity based on the sulfur analysis is 6.79 meq./g.

This new resin is a very strong reducing agent. In the oxidized state it can be reduced only by very strong reducing agents, not by weaker agents as acid-iodide. It is apparently stable to all but strong oxidizing agents such as permanganate. It is also highly specific toward metals which form mercaptides. Detailed experiments will be reported upon later.

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THE SYNTHESIS OF POLY-*p*-THIOLSTYRENE, AN OXIDATION REDUCTION POLYMER

Sir:

We wish to report the successful synthesis of pure poly-*p*-thiolstyrene. This polymer and its copolymers are of both practical and theoretical interest because of the reversible oxidation reduction system of a thiol group and a disulfide group which is the basis for the activity of a number of proteolytic enzymes. In this system disulfide formation provides a labile cross-link. These polymers are also of a potential use as prophylactics for ionizing radiation which are not rapidly excreted from the body.

p-Aminoacetophenone (I) was converted to the xanthate by diazotization followed by reaction with