

water-soluble, polycarboxylic acids.<sup>1</sup> Recent studies in this Laboratory of the reaction products from decarboxylation of the copper salts of these acids have resulted in the recovery of the lactone of 2'-hydroxy-2-biphenylcarboxylic acid (6-dibenzo-pyrone), along with mono- and bicyclic aromatic hydrocarbons. This lactone was characterized by melting point, ultimate analysis, and comparison of infrared spectrum, of ultraviolet spectrum, and of properties of the methoxy acid derivative with those of an authentic sample.

The isolation of this lactone from the oxidation products of coal is highly suggestive in connection with oxidation mechanisms of carbonaceous materials. Lactone rings are very sensitive to pH. In an alkaline hydroxide solution, the ring is opened and the resultant hydroxyl and carboxyl groups will undergo the usual reactions of such groups. In an acid medium, a stable six-membered oxygen-containing ring is formed and further attack on interior rings would be expected to be difficult. The presence of lactones as intermediates would furnish a possible explanation for the much higher rates of oxidation of coals in alkaline than in acid media. Nitric acid is a very effective reagent in the primary stages of the oxidation of coals and various forms of carbon, but to complete the oxidation to benzenecarboxylic acids it has been found advantageous to follow the primary nitric acid oxidation with a secondary one in alkaline medium.<sup>2</sup> The formation of stable lactone rings in the acidic stage would account for such behavior. This lactone of the biphenyl hydroxy acid is relatively insoluble in aqueous sodium carbonate and this fact suggests an explanation for the lower oxidation rates of coal in sodium carbonate compared with sodium hydroxide solutions. The highest methoxyl values for "regenerated humic acids" are obtained by the Wallaschko<sup>3</sup> method, where the compound is dissolved in an excess of alcoholic potash before reaction with dimethyl sulfate. One would expect very complete opening of lactone rings under such circumstances. The esters of acids from oxidation of coal have been shown to form adducts with stannic chloride in dilute pentane solutions. This lactone forms such an adduct under identical experimental conditions.

It has been reported<sup>4</sup> that the rate of reaction of ozone on coal is markedly affected by the presence of water and that the action of this oxidizing agent on "regenerated humic acids" is greatly accelerated if the acids have been previously treated with boiling aqueous alkali. These facts point to a hydrolytic step in the reaction mechanism.

It is well established that the reaction of steam or water with carbon is greatly accelerated by the presence of alkalis; the opening of peripheral lactone rings could be responsible for the effect. It is possible that surface oxygen complexes, such as the  $C_xO_y$  of Rhead and Wheeler,<sup>5</sup> consist in part of

(1) N. W. Franke, M. W. Kiebler, C. H. Ruof, T. R. Savich and H. C. Howard, *Ind. Eng. Chem.*, **44**, 2784-2792 (1952).

(2) B. Juettner, *THIS JOURNAL*, **59**, 208-213 (1937); O. Grossinsky, *Glückauf*, **88**, 988-995 (1950).

(3) N. Wallaschko, *Arch. Pharm.*, **242**, 242 (1904).

(4) C. R. Kinney and L. D. Friedman, *THIS JOURNAL*, **74**, 57-61 (1952).

(5) T. F. E. Rhead and R. V. Wheeler, *J. Chem. Soc.*, **101**, 846 (1918); **100**, 461 (1912).

lactone rings in peripheral positions. That such lactones can be produced by gas phase oxidation has been demonstrated recently by Brooks<sup>6</sup> who obtained this identical lactone by the air oxidation of phenanthrene in a fluidized catalyst bed at 370°.

(6) J. D. Brooks, *Research*, **5**, 196 (1952).

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#### REACTIONS OF ALLYL ALCOHOL-1-C<sup>14</sup>

Sir:

Although an allylic rearrangement would be expected to occur when allyl alcohol is transformed into an allyl halide under certain experimental conditions, the extent to which it takes place has not been determined. In the present work allyl alcohol-1-C<sup>14</sup> was converted to radioactive allyl chloride and allyl bromide by different methods, the starting material and final products degraded with ozone, and the amount of rearrangement determined from the specific activity of the formaldehyde-C<sup>14</sup>.

By modification of the excellent method of Young and Lane<sup>1</sup> carbon-14 labeled allyl bromide was prepared from allyl alcohol-1-C<sup>14</sup>, phosphorus tribromide, and pyridine at -80°. Upon degradation with ozone, the per cent. rearrangement to allyl bromide-3-C<sup>14</sup> was found to be 46%.

Radioactive allyl chloride was made from allyl alcohol-1-C<sup>14</sup> and thionyl chloride by the method of Meisenheimer and Link<sup>2</sup> and the amount of rearrangement to allyl chloride-3-C<sup>14</sup> was 51%.

Finally, the tosylate of allyl alcohol-1-C<sup>14</sup> was treated with sodium bromide in a suitable solvent and only allyl bromide-1-C<sup>14</sup> resulted indicating no rearrangement.

Further study is in progress with allyl alcohol-1-C<sup>14</sup> and allyl bromide-1-C<sup>14</sup> to determine if in those cases where rearrangement occurs a unimolecular process of replacement involving the formation of a resonating cation is the predominant mechanism.

(1) W. G. Young and J. F. Lane, *THIS JOURNAL*, **59**, 2051 (1937).

(2) J. Meisenheimer and J. Link, *Ann.*, **479**, 211 (1930).

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#### ENZYMATIC SYNTHESIS OF D-GLUTAMINE AND RELATED HYDROXAMIC ACIDS

Sir:

The mechanism of the enzymatic interaction of ATP,<sup>1</sup> L-glutamate, and ammonia, yielding ADP, L-glutamine, and inorganic phosphate has been of interest since the reaction was first described by Speck<sup>2</sup> and by Elliott.<sup>3</sup> Elliott,<sup>4</sup> using a highly purified enzyme from peas, was unable to separate glutamine synthesis from glutamotransferase ac-

(1) Abbreviations employed: ATP = adenosine triphosphate, ADP = adenosine diphosphate, tris = tris-(hydroxymethyl)-amino-methane.

(2) J. F. Speck, *J. Biol. Chem.*, **168**, 403 (1947); **179**, 1367, 1405 (1949).

(3) W. H. Elliott, *Nature*, **161**, 128 (1948).

(4) W. H. Elliott, *J. Biol. Chem.*, **801**, 681 (1953).