ered unchanged in quantitative yield. The second crop of crystals from the reaction of the *i*-ether had the properties of a mixture, indicating incomplete conversion and/or competition between methoxyl and propoxyl groups.

The preparation of cholesteryl halides from the *i*-ether and hydrogen halides under mild conditions[3] is not without analogy to the above. Wallis and co-workers, who have presented the currently most reasonable structure for the *i*-cholesterol compounds, considered[3c] that the interesting formation of the *i*-cholesterol compounds from the tosyl ester of cholesterol could best be described by a formulation which involves a molecular rearrangement. The essential nature of the reaction would now appear to involve an electronic shift between rings A and B with carbon atom no. 5 as the pivot.

A detailed description of the work which assumes interest as a preparative method as well as a presumptive route to the introduction or removal of labels in biochemical work will be reported later.

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RECEIVED AUGUST 21, 1947

FORMATION OF QUINONE BY THE ACTION OF BROMINE OXIDE ON BENZENE

Sir:

In an attempt to elucidate the mechanism of the effect of oxygen in accelerating the bromination of hydrocarbons, the effect of bromine oxide (Br_2O) on the bromination of toluene and cyclohexane was investigated. This substance proved to be a powerful inhibitor for the photobromination of toluene (one mole per cent. of Br_2O in Br_2 reduced the rate of bromination to one-half; two and a half mole per cent. reduced the rate to 1/30). It showed no similar effect on cyclohexane. By comparing the total bromine content of the solution with its oxidizing power as determined by a titration with sodium arsenate, it has been shown that when bromine oxide (Br_2O), dissolved in carbon tetrachloride is mixed, in the light or in the dark, with toluene or cyclohexane, it is decomposed within one or two minutes. Attempts were then made to isolate the compounds formed by the reaction of bromine oxide with the hydrocarbons. When the unreacted bromine and excess solvent were removed from the reaction mixture containing toluene, a yellow concentrate was obtained which acted as an inhibitor in the bromination of toluene. It liberated iodine from acidified potassium iodide and reduced Tollens reagent instantaneously at room temperature. This behavior suggested a quinone. However, all attempts to isolate toluquinone failed.

When benzene was used, the yellow oil (which remained after the removal of the solvent and unreacted materials) liberated iodine from potassium iodide, reduced Tollens reagent, and had a characteristic quinone odor. The material was molecularly distilled at reduced pressure. The yellow crystals, thus obtained, melted at 111–113°, and did not depress the melting point of an authentic sample of *p*-benzoquinone. The residue still reduced Tollens reagent and liberated iodine from potassium iodide. It was moderately soluble in water in which it formed a pink solution, suggestive of *o*-benzoquinone; but attempts to isolate this compound have thus far met with no success.

The direct formation of quinone from benzene is most remarkable. It is one of the few instances known to the authors, whereby, in a single reaction, benzene is converted to quinone. The study of other halogen oxides is contemplated.

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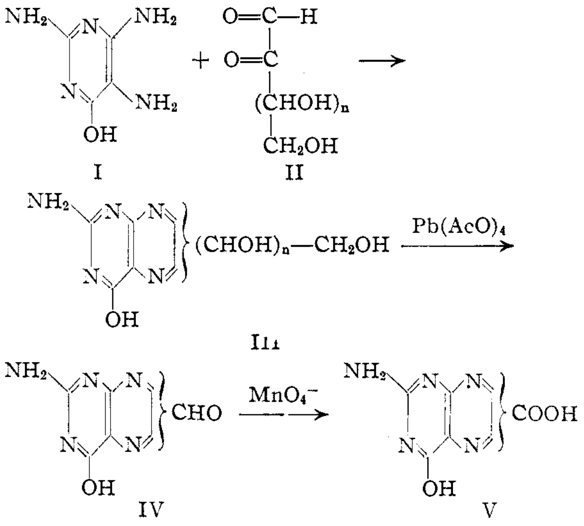
RECEIVED OCTOBER 6, 1947

A NEW SYNTHETIC METHOD FOR PTERINES

Sir:

In view of the recent publication of Karrer, *et al.*,[1] on the synthesis of polyhydroxypterines by the condensation of sugars with 2,3,5-triamino-6-hydroxypyrimindine (I) we wish to report our observations on the same reaction and on a new synthesis for similar compounds which is outlined below.



In our hands the condensation of D-glucose with I under the conditions of Karrer, *et al.*, yields 7-tetrahydroxybutylpterine, while the condensation of D-glucose with I-bisulfite or I-bisulfate under strongly acidic conditions yields primarily 6-tetrahydroxybutylpterine. The type of isomer obtained is determined by the physical properties of III or the carboxy-pterine (V) obtained from it.

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[1] Karrer, Schwyzer, Erden and Siegwart, *Helv. Chim. Acta*, **30**, 1031 (1947).