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THE ADDITION REACTIONS OF VINYL PHENYL KETONE, III.
MALONIC ESTER.

A new apparatus has been devised and a procedure developed for the preparation of β -chloropropiophenone by the Friedel-Crafts reaction from benzoyl chloride and ethylene. Methyl malonate has been added to vinyl phenyl ketone thus forming methyl γ -benzoyl ethyl malonate (I), which on hydrolysis and decarboxylation gave the known γ -benzoylbutyric acid. The ester (I) was brominated and from the oily bromoester by removal of hydrogen bromide methyl 2-benzoylcyclopropane-1, 1-dicarboxylate was produced. The properties of this ester, the corresponding dibasic acid (II), and two stereoisomeric cyclopropane monobasic acids and a lactone produced on pyrolysis of (II) have been studied. The structure of the lactone was established by synthesis. In agreement with other ketonic cyclopropanes of similar type, the ring was only opened between the 1 and 2 ring carbon atoms. This is in contrast with ketonic cyclopropanes having a phenyl group in the 3 position.

PH. D.

EXPERIMENTAL MEDICINE

ELIZABETH RHODA GRANT

STUDIES IN GLYCOGEN METABOLISM.

The recovery changes following artificially-induced exercise have been studied in the intact white rat in the 24-hour fasted and post-absorptive conditions, with the aim of testing the hypothesis, founded on isolated frog muscle experiments, that, except for a small fraction, the lactic acid produced from glycogen is resynthesised to glycogen during oxidative recovery.

The results show that the muscle glycogen restoration is dependent on the availability of liver glycogen. Failing this the only restoration possible appears to be brought about by a slowly working mechanism such as maintains equilibrium close to the 24-hour fasted level.

The "oxidation quotient" determined directly in the intact rat during exercise has been found to have a value of 3 to 5, in agreement with values found during recovery in isolated muscles and in man.

Phlorhizin experiments, which failed in their original purpose, are reported for their interest in connection with the transformation of fat to carbohydrate.

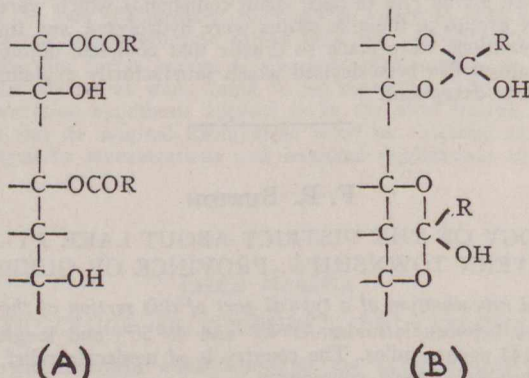
PH. D.

CHEMISTRY

MARGARET ELIZABETH GREIG

STUDIES IN HYDROGEN MIGRATION.

It was assumed that in the interaction of one mole of an acid and one mole of a 1:2 or 1:3 glycol the resulting mono ester should represent an equilibrium mixture of the open chain ester (A) and the dioxolane or dioxane ring (B)



the amount of (A) or (B) present depending on the polar character of the carbonyl group. The existence of the cyclic forms has been confirmed in the case of various esters of trichloroacetic acid. It was found that with trichloroacetic acid the main product formed with ethylene glycol, glycerol monomethyl ether, trimethylene glycol, β - β dimethyl propylene glycol, was the ring compound and not the open chain ester. These ring structures correspond to the intermediate products formulated by Emil Fischer to explain the mechanism of acyl migration. The cyclic structure was proved by preparing the methyl ethers of the dioxolane or dioxane derivatives and showing that their properties were very different from those of the isomeric open chain monomethyl ethers.