COMMUNICATIONS TO THE EDITOR

REACTIONS OF CYCLOHEXANONE WITH DIAZOETHANE

Sir:

It has been shown by Mosettig and Burger [THIS JOURNAL, **52,** 3456 (1930)] and by Meerwein (German Patent 579,309) that cyclohexanone reacts with diazomethane to form cycloheptanone and cyclooctanone as main products. The reaction takes place slowly even in the presence of a catalyst. Mosettig and Burger have suggested the possibility of replacing diazomethane by diazoethane and its homologs in this reaction.

In an investigation of the reactions of cyclic ketones with diazomethane and similar compounds which is under way in this Laboratory, the reaction of cyclohexanone with diazoethane has been carried out and the product obtained proved to be α-methylcycloheptanone. It was identified as the semicarbazone, m. p. 128–129°. Isolation of the product was brought about by removing the unattacked cyclohexanone with bisulfite solution, methylcycloheptanone being unaffected by this reagent. In contrast to the reaction with diazomethane, diazoethane requires no catalytic influence and the reaction is completed in a much shorter period of time. The reaction with diazomethane requires several days for completion while that with diazoethane takes less than twenty-four hours.

It is interesting further to record that while diazomethane reacts readily with cyclohexanone to form both cycloheptanone and cyclooctanone, according to the conditions of the reaction, it is without effect on cycloheptanone and reacts to a slight extent only with cyclopentanone, the products being mainly cycloheptanone together with a small amount of cyclohexanone.

In order to obtain information on the behavior of substituted cyclic ketones toward diazomethane and diazoethane reactions have been carried out with α-chlorocyclohexanone. Diazomethane gave practically a quantitative yield of α-chlorocycloheptanone while diazoethane gave methylchlorocycloheptanone as the main product.

These reactions were carried out in ether solution. The ketone was added to the ethereal solution of diazomethane or diazoethane and if evolution of nitrogen did not occur immediately methyl alcohol was added to catalyze the reaction. Completion of the reaction was indicated by disappearance of the yellow color in the solution.

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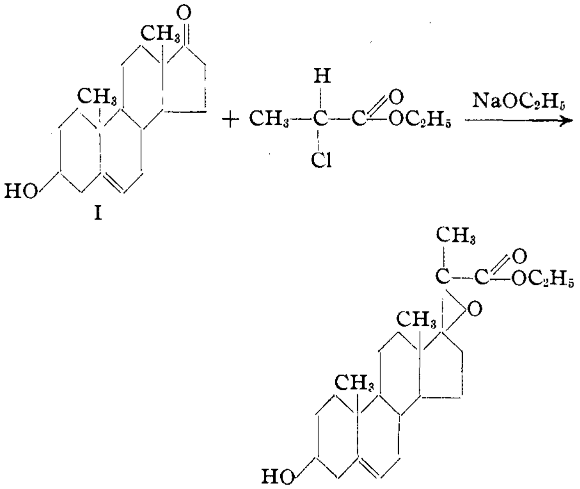
THE CONDENSATION OF DEHYDROANDROSTERONE WITH ETHYL α-CHLOROPROPIONATE

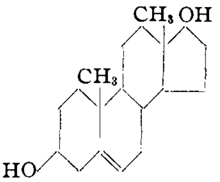
Sir:

In the course of certain studies on the chemical properties of dehydroandrosterone, I, we have observed that under suitable conditions, in the presence of sodium ethylate, it is possible to effect a condensation of the Darzens type [*Compt. rend.*, **141,** 766 (1906)] between this hormone and ethyl α-chloropropionate according to the scheme

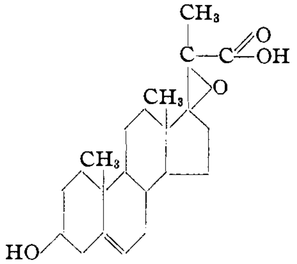


II

Some androstenediol-(3,17), III, is also formed during the reaction by the reducing action of the sodium ethylate. We have also found that hydrolysis of the ester oxide, II, with sodium hy-



III



IV