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 cycloöctanone 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 cycloöctanone, 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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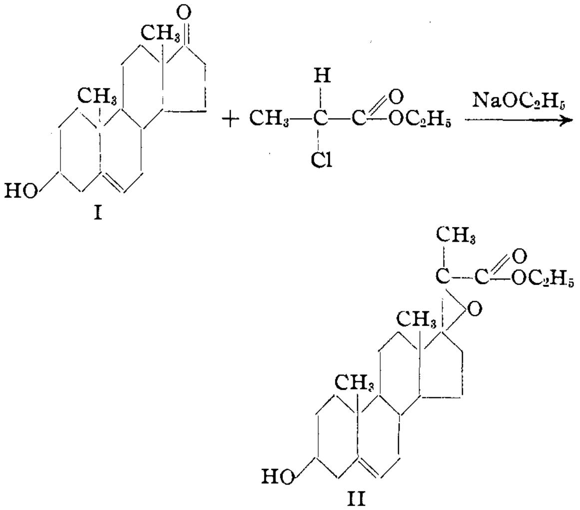
RECEIVED MARCH 26, 1937

THE CONDENSATION OF DEHYDROANDROSTERONE WITH ETHYL α-CHLOROPROPIONATE

Sir:

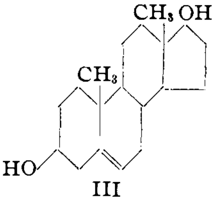
In the course of certain studies on the chemical properties of dehydroandrosterone, I, we have observed that under suitable conditions, in the presence of sodium ethylate, it is possible to effect a condensation of the Darzens type [*Compt. rend.*, **141,** 766 (1906)] between this hormone and ethyl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



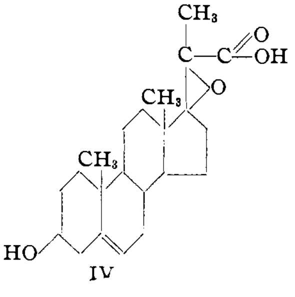
I

II

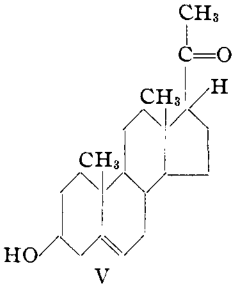
Some androstenediol-(3,17), III, is also formed during the reaction by the reducing action of the sodium ethylate. We have also found that hydrolysis of the ester oxide, II, with sodium hy-



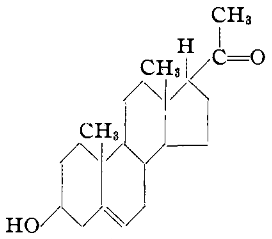
III



IV



V



VI

droxide yields two products: (a) an acid which forms an insoluble sodium salt, and presumably has the formula IV; and (b) a mixture of ketones formed by a rearrangement process having properties of Δ^5-pregnenolone, V, and Δ^5-*iso*-pregnenolone, VI, previously prepared from stigmasterol and pregnanediol by Fernholz [*Ber.*, **67**, 1855, 2027 (1934)] and by Butenandt and his co-workers [*Ber.*, **67**, 1611, 1901 (1934); **70**, 96 (1937)]. The exact proportions of the two ketones in the mixture are now being investigated, and experimental studies on the rearrangement of the acid, IV, into the corresponding ketones are in progress. The details of our experimental results will be published in a forthcoming paper. We hope that this announcement may serve as a reservation of this research project.

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NEW BOOKS

Alchemy and Other Chemical Achievements of the Ancient Orient. The Civilization of Japan and China in Early Times as Seen from the Chemical Point of View. By Dr. MASUMI CHIKASHIGE, Emeritus Professor of Kyoto Imperial University. Rokakuho Uchida, Tokyo, Japan, 1936. 102 pp. 17 plates. 12.7 × 18.8 cm. Price, 1.50 Yen.

This is an English translation of a book which appeared in the Japanese language in 1929 under a title which may properly be translated "Metallurgic Arts in the Orient." The Japanese version contained a discussion of European alchemy which is omitted from the present translation. The work is divided into three parts which deal, respectively, with Chinese alchemy, with Chinese bronze and with Japanese steel swords.

The author considers that many alchemical books can be enumerated, but that "in the final analysis, only two works, *Pao-p'u-tzu* (written by *Ko Hung*, fourth century A.D.) and *Pên Ts'ao Ching*" (a treatise on materia medica published toward the end of the *Han* dynasty) "remain as the authentic sources of information on the earlier Chinese alchemy." Biographical accounts of *Ko Hung* and *T'ao Hung-ching* are given, and many interesting quotations from the second (*Lun Hsien*, "Essay on the Immortals"), the fourth (*Chin Tan*, "Gold Medicine"), the eleventh (*Hsien Yao*, "Medicines of the Immortals") and the sixteenth (*Huang Pao*, "The Yellow and the White") of the Inner Chapters of "*Pao-p'u-tzŭ*." Chikashige discusses the identity of some of the materials which *Ko Hung* used, and concludes that some of the processes may actually have yielded real gold because of the gold which existed in small amounts in the reagents.

The discussion of ancient Chinese bronzes centers around the "Six Recipes of *Chin*" which are set down in the *Chou Li K'ao Kung Chi* (Artificers' Record, the sixth part of the *Chou* ritual) which was published during the *Chou* dynasty in the tenth century B.C. The author concludes that these recipes, except the last one, are reasonable. He discusses the properties of the several kinds of bronze which correspond to them, and finally reports chemical analyses of ancient bronzes in which the proportions of copper to tin agree with those laid down in certain of the recipes. He has wisely made his analyses upon the uncleaned bronze objects, determining the total amount of each metal present in the combined mass of metal and oxidized material.

"As to the method of forging swords in extreme antiquity, no history nor tradition has been handed down; but some of the straight swords excavated by archeologists were once submitted to investigation from which it may be concluded with some justice that they belong to the class of forged swords. For they showed some signs of having been forged by 'folding,' or even by 'combining' different sorts of iron. The art of forging made great progress when in the days of the Prince Regent *Shōtoku* (573–621) it was taught by some naturalized smiths at Oshinumi and later when Emperor *Gotoba* (1180–1239) gave directions to the noted smiths of the various provinces and made them forge at the court. All this concerns the method of forging the so-called *kotō* (old swords) but this method was lost during the age of civil wars toward the end of the *Ashikaga* Period. *Shintō* (new swords) made their first appearance toward the beginning of the *Tokugawa* Period and during the *Anei* (1772–1780) era or thereabouts *shinshintō* (new new swords) began to be turned out. A sword-smith, named *Suishinshi* is said to have been the originator of the *shinshintō* school. He was a diligent investigator of the oldest school of sword forging, and thus the once obscured method became clear again; but it did not live long as such, for *Suishinshi* improved it further and gave birth to a new school. The doctrine of the school of *shinshintō* still survives among the sword-smiths of the last days of the *Tokugawa* Period."