

been described in THIS JOURNAL, 54, 4116 (1932), and *Ind. Eng. Chem., Anal. Ed.*, 4, 342 (1932).]

Secondary alcohols also undergo hydrogenolysis but in this case the reaction involves the cleavage of a carbon to oxygen rather than a carbon to carbon bond, *i. e.*, $R_2CHOH + H_2 = R_2CH_2 + H_2O$. This type of reaction giving a hydrocarbon of the same carbon content as the alcohol is not novel; in fact it has been regarded as the normal reaction for primary as well as secondary and tertiary alcohols. The reaction proceeds smoothly under the conditions described above. For example, cyclohexane (m. p. 4–5°, n_D^{25} 1.4260) and *n*-octane were the only hydrocarbons obtained by the hydrogenolysis of cyclohexanol and octanol-2.

The primary-secondary glycol octadecanol-1,12, $CH_3(CH_2)_5CHOH(CH_2)_{10}CH_2OH$, as would be anticipated from the results stated above, underwent carbon to oxygen cleavage at the secondary carbinol, and carbon to carbon cleavage at the primary carbinol, with the formation of *n*-heptadecane, $C_{17}H_{36}$. The glycol [293 g., m. p. 67–69°, b. p. 200–208° (4 to 5 mm.)] was obtained by hydrogenation of castor oil (500 g.) over copper-chromium oxide catalyst (35 g.) for nine hours at 250° under 200–300 atmospheres pressure. The product so obtained was not completely homogeneous, as evidenced by its physical constants and the fact that in addition to the main product, *n*-heptadecane, a small amount of an unidentified hydrocarbon was obtained in its hydrogenolysis.

The primary alcohols and decanediol-1,10 subjected to hydrogenolysis were prepared from the ethyl esters of the corresponding acids through the action of hydrogen over a copper-chromium oxide catalyst [THIS JOURNAL, 54, 4678 (1932)]. Both of the steps in the conversion of an ester to a hydrocarbon containing one less carbon atom than the acyl group of the ester can be accomplished by using a mixture of the two catalysts, *i. e.*, copper-chromium oxide and nickel. However, our experience indicates that it is preferable to carry out the operation in two stages since the water formed in the second step prevents the completion of the first reaction.

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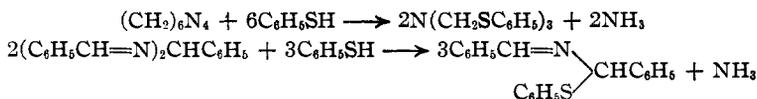
A NEW CONDENSATION REACTION OF THE THIOPHENOLS

Sir:

In view of the recent increase of interest in mercaptan chemistry, both in this country and abroad, we should like to report briefly upon a new reaction of the thiophenols, the investigation of which has been carried forward in this Laboratory during the past two years.

We have found that phenyl mercaptan itself, and many substituted

thiophenols, as well as benzyl mercaptan, undergo condensation in boiling 1,4-dioxane solution with such condensed ammonia-aldehydes as hexamethylenetetramine and hydrobenzamide, only part of the nitrogen of the base being eliminated as ammonia. The products are crystalline substances (except in a very few cases) which may be considered as substituted trimethylamines. The following typical examples of the reaction will serve to illustrate



The only analogous reactions which we have been able to find reported in the literature are those of hexamethylenetetramine with such weak acids as HCN [Eschweiler, *Ann.*, **278**, 230 (1894)] and N-nitromethylamine [Franchimont, *Rec. trav. chim.*, **29**, 355 (1910)], where a similar condensation takes place.

We are continuing our investigations and hope very shortly to be able to publish a detailed report of the work.

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ON THE MAXIMUM ROTATIONS IN THE HOMOLOGOUS SERIES OF α -BROMO ACIDS

Sir:

In the course of our work on the shift of the molecular rotations of members of homologous series, we were in need of resolving α -bromobutyric and α -bromocaproic acids to the maximum. The α -bromopropionic acid had already been resolved to the maximum of $[\text{M}]_D^{25} - 43.6^\circ$ by Ramberg [*Ann.*, **370**, 234 (1909)] through the cinchonine salt.

We succeeded in resolving the α -bromobutyric acid through its brucine salt to $[\text{M}]_D^{25} + 59.62^\circ$ and α -bromocaproic acid through its strychnine salt to $[\text{M}]_D^{25} - 71.45^\circ$, thus showing that in this homologous series the values of the rotations of the individual members increase progressively. The progress in the case of the methyl esters was similar, being 83, 92 and 104° , respectively, for the three esters.

These results were obtained nearly a year ago and remained unpublished for the reason that they were intended to be part of a comparative study of the rotations of the corresponding α -hydroxy and α -amino acids.

We wish to record the results at this time for the reason that in the current number of the *Journal für praktische Chemie* there appeared an article by Ahlberg [*J. prakt. Chem.*, **135**, 335 (1932)] devoted exclusively to the