

THE REACTION BETWEEN NEUTRAL LEAD MERCAPTIDES AND SULFUR

Sir:

The reaction between neutral lead mercaptides and sulfur in benzene solution leads to the formation of lead disulfide and organic polysulfides [W. E. Duncan and Emil Ott, *THIS JOURNAL*, **53**, 3940 (1931)].

Preliminary work on the similar reaction with basic lead mercaptides indicated an analogous reaction with the formation of basic lead polysulfides of the type $\text{HOPbS}_x \cdot \text{PbOH}$ [Emil Ott and E. E. Reid, *Ind. Eng. Chem.*, **22**, 884 (1930); **22**, 878 (1930)].

This reaction was now studied more extensively with basic *sec.*-butyl lead mercaptide. The relatively stable yellow-orange (light reddish-brown when dry) precipitate obtained by the addition of sulfur in benzene solution was definitely established to be a mixture of basic lead polysulfides of the type mentioned above. Most mixtures may simply be described as containing the compounds with $x = 3$ and $x = 4$, but in some cases $x = 5$ is additionally present.

Thorough qualitative tests and quantitative analyses for lead, sulfur, hydrogen and carbon established composition and constitution of the products.

Since the basic *sec.*-butyl lead mercaptide cannot be prepared entirely free from neutral *sec.*-butyl lead mercaptide, a certain amount of lead disulfide is also formed, the amount of which can be predicted accurately from the analysis of the mercaptide solution. Thus no uncertainty is introduced into the final analyses. It lies in the nature of the problem that no individual compounds could be isolated; for the same reason this abbreviated communication seemed necessary.

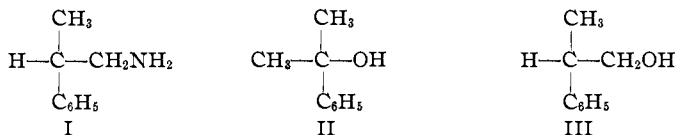
DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
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WALLACE E. DUNCAN
EMIL OTT

REARRANGEMENTS BY THE ACTION OF NITROUS ACID ON AMINES OF THE TYPE $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{NH}_2$

Sir:

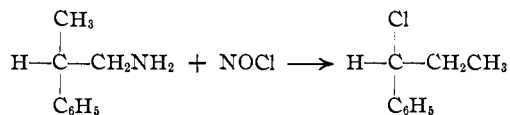
The amine I on treatment with nitrous acid should form, on the basis of observations made on aliphatic amines of this type, two isomeric carbinols,



II in predominating proportion and III in much smaller proportion. In the case of the optically active amine, the first carbinol should be optically

inactive. Similar effects should be expected from the action on the amine of NOCl or NOBr. The active halides should be expected to be the primary. This assumption was made by Levene, Mikeska and Passoth [*J. Biol. Chem.*, **88**, 27 (1930)] and was made the basis of the correlation of the substituted phenylacetic to phenylpropionic acids by Levene and Marker [*ibid.*, **93**, 749 (1931)].

We now find that the active halide obtained by the action of nitrosyl halides on the amine is not a primary but a secondary halide. Thus, in course of the reaction an unexpected rearrangement takes place



inasmuch as this halide leads to $\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\text{C}-\text{C}_2\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \end{array}$.

A similar rearrangement takes place in the case of 1,1-ethylphenylethylamine (Ref. 2).

It may be mentioned here that the dextrorotatory substituted phenylacetic acids are now correlated to levorotatory substituted 3-phenylpropionic acids on the basis of new evidence. The details will be published in the *Journal of Biological Chemistry*.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

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P. A. LEVENE
R. E. MARKER
ALEXANDRE ROTHEN

THE COLORIMETRIC DETERMINATION OF FLUORINE IN WATER WITH FERRIC THIOCYANATE

Sir:

In the determination of fluorine in water it has been found most satisfactory to use a colorimetric method based on the fact that the complex ion formed in the reaction between a fluoride and ferric chloride does not give the characteristic iron color with ammonium thiocyanate. Thus, with more iron than is necessary to react with the fluoride, the color is less than that produced by the same amount of iron without fluoride. By determining colorimetrically the quantity of iron reacting with the ammonium thiocyanate, the quantity withdrawn by the fluoride may be found by difference and its equivalent in fluoride read from a curve which has been made by plotting the effect of definite amounts of fluoride upon the amount of iron used in the determination.

The alkalinity of the sample of water must be neutralized and if the volume of the sample is much over 50 cc., it must be evaporated to about