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## Addition of Chloroamines to Ketenes

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HEAVY WATER OBTAINED BY THE COMBUSTION OF  
DRIED BIOLOGICAL SPECIMENSH. L. KEIL, A. W. RALSTON, M. T. KELLEY, W. E. CATLIN,  
W. H. JENNINGS, J. STRALEY AND H. GILMAN

Dry, finely divided plant and animal tissues were oxidized by passage over hot copper oxide; the aqueous condensates were first distilled from potassium permanganate and then alone. If necessary, oxidation and distillation were repeated until there was no significant change in density. Densities were determined by a modification of the submerged magnetic float procedure, and the accuracy was one part per million. The specimens examined were practically all of the chief organs of cattle; yeasts; dairy products; and some parts of plants like corn and melons. The study is being extended to other biological specimens, normal and pathological.

CHEMICAL RESEARCH DEPARTMENT OF  
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## ADDITION OF CHLOROAMINES TO KETENES

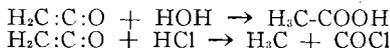
GEORGE H. COLEMAN AND ROLF L. PETERSON

Considerable work has been done in this laboratory on the reactions of chlorine derivatives of nitrogen compounds, particularly nitrogen trichloride, monochloroamine, monobromoamine, dibromoamine, and the alkylchloroamines.

Nitrogen trichloride adds to unsaturated hydrocarbons, unsaturated ketones, and unsaturated acids, to form C-chloro-N-dichloroamino derivatives. The products formed in these addition reactions of nitrogen trichloride indicate that the -Cl is apparently more electropositive than the -NCl<sub>2</sub> group.

Monochloroamine and substituted chloroamines do not add to unsaturated hydrocarbons, ketones, or acids. This method of determining what might be called the relative electro-negativity or perhaps the electron sharing ability of the atoms or radicals involved is therefore not available.

Since the ketenes are very reactive compounds and react with given reagents as illustrated in the following equations



it seemed probable that they would be valuable reagents in the study of the character of the chlorine in monochloroamine and substituted chloroamines.

In the present work monochloroamine has been found to add to diphenyl ketene to form diphenylchloroacetamide, a result which is in agreement with the assumption that a chlorine attached to nitrogen displays an electropositive character in reactions. However the addition of monochloroamine to unsubstituted ketene formed N-chloroacetamide. In order to study the problem further, the reactions of dimethylchloroamine with both ketene and diphenyl ketene have been tried. N-dimethylchloroacetamide and N-dimethyldiphenylchloroacetamide, respectively, were formed in these reactions.

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## IDENTIFICATION OF HYDRAZONES AND ISOMERIC PYRAZOLINES OBTAINED FROM $\alpha$ , $\beta$ -UNSATURATED KETONES

WALTER J. PETERSON AND L. CHAS. RAIFORD

To date there are but two methods for distinguishing between these compounds. The first involves the reduction of the hydrazone with sodium amalgam to give aniline and the corresponding aliphatic amine. The yields are low and many cases tried have given negative results. The pyrazolines do not suffer this change. The second method is based on the fact that many of these hydrazones are rearranged by boiling acetic acid to the isomeric pyrazolines. If, in this way, the compound in question is converted into a new product, the latter is probably, but not certainly, a pyrazoline. If the latter can be oxidized to benzoic and a pyrazole acid, the pyrazoline is more clearly indicated.

It has now been shown that the differences between the crystalline shapes of these isomers may be utilized in some cases to distinguish them. Likewise, it has been found that reduction by sodium amalgam in the presence of carbon dioxide as directed by Schlenk<sup>1</sup> saturates only the ethylenic linkages, and that the result-

<sup>1</sup> *J. pr. Chem.* (2) 78, 57 (1908).