

quite analogous to that of the aldehyde group in the above cases. The difference, emphasized by Kohler and Potter, between mesitylenic and phenyl ketones shows that the electromeric effect of the keto group in the former is much stronger and near to that of the aldehyde group. The writer has no explanation to offer for this new and remarkable fact, but he wishes to point out that he has not attempted theoretically to explain the relative strengths of the electromeric effects even of the simple groups investigated by him, which were only classified according to experimental evidence.

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A Crystalline Compound of Semicarbazide and Semicarbazide Hydrochloride

BY H. L. HALLER AND F. B. LAForge

In preparing semicarbazones of the pyrethrins and related compounds in this Laboratory it was found¹ that the substitution of pyridine for sodium acetate increased the rate of reaction and resulted in much better yields of the semicarbazones. While using this procedure it was observed that sometimes crystals were deposited immediately from the solution. However, this did not occur in all cases. That this is not due to the formation of a semicarbazone is evidenced by the fact that the same material was sometimes obtained when a concentrated aqueous solution of semicarbazide hydrochloride was added to a mixture of pyridine and ethanol in the absence of ketones. Whether or not the crystallization occurred was found to depend upon the amount of water in the system. The crystalline product was always obtained when 2.5 g. of semicarbazide hydrochloride in 2.5 cc. of hot water was added to 17 cc. of 95% ethanol and 3 cc. of pyridine. The compound appears in the form of large prisms which are almost insoluble in alcohol and in pyridine but are easily soluble in water and aqueous alcohol provided the amount of water exceeds about 10%. It contains ionic chlorine and may be titrated with standard alkali solution. It melts at 132°.

Anal. Calcd. for $C_2H_{11}N_6O_2Cl$: equiv. wt., 186.5; N, 45.05; Cl, 19.03. Found: (36.8 mg. required 2.01 cc. of 0.1 *N* potassium hydroxide so-

(1) H. L. Haller and F. B. LaForge, *J. Org. Chem.*, **1**, 38 (1936).

lution) equiv. wt., 183.1; N (Dumas), 45.06; Cl, 18.85.

This empirical formula is satisfied by the postulation that the compound contains one molecule of semicarbazide and one molecule of semicarbazide hydrochloride.

When the compound is dissolved in a small quantity of warm concentrated hydrochloric acid, the solution on cooling deposits semicarbazide hydrochloride, decomposing at 176°.

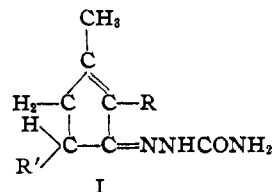
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The Solubility of Certain Semicarbazones in Dilute Hydrochloric Acid

BY F. B. LAForge AND H. L. HALLER

In our investigations of the constituents of pyrethrum flowers, the semicarbazones of the pyrethrins and related compounds have served for their isolation and identification. Although pyridine has been substituted in all cases for the more commonly used sodium acetate in preparing these semicarbazones,¹ the employment of this base has had no effect on the properties of the derivatives obtained. Semicarbazones have been classed as neutral compounds, and those that are not soluble in water are supposed to be insoluble in dilute acids and alkalis.

In working with the semicarbazone of tetrahydropyrene (dihydrojasnone), formula I, $R = C_6H_{11}$, $R' = H$, we first observed that it was easily dissolved in cold dilute hydrochloric acid (about 4 *N*).



In the acid solution the semicarbazone is, of course, hydrolyzed on long standing and rapidly at elevated temperatures. It is, however, precipitated unchanged and in quantitative yield from the cold solution by prompt addition of alkali.

We were led by this observation to examine other related semicarbazones and have found

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