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.

DEPARTMENT OF GENERAL CHEMISTRY
UNIVERSITY OF ISTANBUL
ISTANBUL, TURKEY RECEIVED JANUARY 21, 1937

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 found[1] 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 solution) 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°.

CONTRIBUTION FROM THE
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C. RECEIVED FEBRUARY 11, 1937

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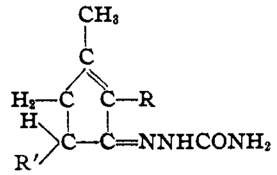
[1] H. L. Haller and F. B. LaForge, *J. Org. Chem.*, **1**, 38 (1936).

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 alkalies.

In working with the semicarbazone of tetrahydropyrethrone (dihydrojasmone), formula I, R = C_5H_{11}, R′ = H, we first observed that it was easily dissolved in cold dilute hydrochloric acid (about 4 N).



I

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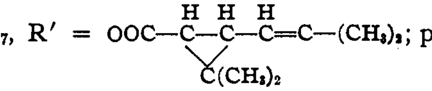
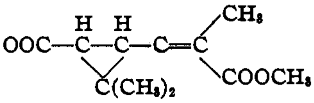
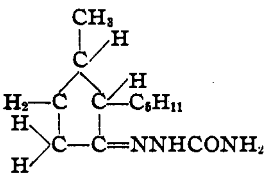
[1] H. L. Haller and F. B. LaForge, *J. Org. Chem.*, **1**, 38 (1936).

them to differ sharply with respect to their solubility in acids. The semicarbazones which we have considered may be divided into two groups, those that are soluble and those that are insoluble in dilute hydrochloric acid.

The former include the semicarbazones of pyrethrone, formula I, R = C_5H_7, R′ = H; dihydropyrethrone (jasmone), R = C_5H_9, R′ = H; tetrahydropyrethrone (dihydrojasmone), R = C_5H_{11}, R′ = H; and tetrahydropyrethrolone, R = C_5H_{11}, R′ = OH. The acid-insoluble semicarbazones include those of pyrethrolone, formula I, R = C_5H_7, R′ = OH; pyrethrin I, R = C_5H_7, R′ =  $\mathrm{OOC-\underset{\diagdown C(CH_3)_2\diagup}{\overset{H}{C}-\overset{H}{C}}-\overset{H}{C}=C-(CH_3)_2}$; pyrethrin II, R = C_5H_7, R′ =  $\mathrm{OOC-\underset{\diagdown C(CH_3)_2\diagup}{\overset{H}{C}-\overset{H}{C}}-C=C\begin{smallmatrix}\diagup CH_3\\ \diagdown COOCH_3\end{smallmatrix}}$ and two geometric forms of hexahydropyrethrone semicarbazone of melting points 160 and 194°, respectively, represented by formula II.



II

There seems to be no chemical feature distinguishing the members of each group. The solubility of some of the semicarbazones has been utilized in their separation from other material. All of an acid-soluble semicarbazone present in an impure reaction mixture may be obtained practically pure by extraction with dilute hydrochloric acid, removal of the by-products with a water-immiscible solvent, and precipitation of the semicarbazone with alkali. For example, a reaction product consisting of tetrahydro- and hexahydropyrethrone semicarbazones was separated into the two components by dissolving the one in dilute acid and filtering from the other.

To what extent the property of solubility in hydrochloric acid is shared by the semicarbazones of other ketones is a matter of interest, but one which we have not investigated.

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Photoreaction of Chlorine Monoxide and Hydrogen

BY T. IREDALE AND T. G. EDWARDS

According to Finkelnburg, Schumacher and Stieger[1] chlorine monoxide dissociates, in the continuous absorption region of the visible spectrum, into Cl and ClO. We have found that addition of hydrogen accelerates the decomposition, at any rate, up to the stage where the secondary reaction $H_2 + Cl_2 = 2HCl$ becomes prominent. As without the H_2, Cl_2 and O_2 are the main products, but there are now also small amounts of HCl and H_2O. Finally all the Cl_2 goes to HCl.

Since the reaction $Cl + H_2 = HCl + H$ has a collision efficiency of $10^{-4} - 10^{-5}$, and $Cl + Cl_2O = Cl_2 + ClO$[1] a collision efficiency of $10^{-2} - 10^{-3}$, H atoms are not so important as the ClO radical in continuing the chain, that is, where the Cl_2O and H_2 pressures are comparable. The chain must, therefore, be continued by the reactivity of ClO and H_2, a state of affairs not much understood in the literature of this subject.

We may have either $ClO + H_2 = HClO + H$ or $ClO + H_2 = HCl + OH$. The latter reaction seems the more probable. Further details will be forthcoming when we have studied the reaction more closely.

Contrary to the experience of others,[2] we did not find that Cl_2O was explosively unstable in the presence of strong light. A 500 candle power lamp brought within 2.5 cm. of a spherical glass bulb (7.6 cm. in diameter) containing Cl_2O at a pressure of half an atmosphere, did not cause an explosion, nor did it do so when hydrogen was present at the same pressure.

[1] Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **B15**, 127 (1931).

[2] Wallace and Goodeve, *Trans. Faraday Soc.*, **27**, 653 (1931).

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The Heat of Mixing of Diisobutylene and Isooctane

BY WM. D. KENNEDY AND GEORGE S. PARKS

In connection with the recent study by Crawford and Parks[1] of the liquid-phase hydrogenation of diisobutylene (*i. e.*, a material containing about 4 parts of 2,4,4-trimethylpentene-1 and 1 part

[1] B. L. Crawford and G. S. Parks, THIS JOURNAL, **58**, 373 (1936).