distillation to dryness at reduced pressure to give 19.1 g. of residue. The residue was dissolved in a small amount of water, the solution heated with charcoal to 100°, the charcoal removed and the solution again subjected to distillation to dryness at reduced pressure to give 18.7 g. of residue. Several recrystallizations from 95% alcohol gave successively 8.0 g. of crystals, m. p. 119–121.5°; 2.5 g., m. p. 118–121°; and 0.2 g., m. p. 118–120.5°; a total yield of 10.7 g. The total volume of solution in the reported high pressure experiment was 179 cc., but since 12 cc. of this solution had been used for analyses, the maximum possible yield was 17.8 g. Erythritol was therefore isolated in 60.1% yield.

Summary

1. The method of catalytic hydrogenation at high pressures has been applied to two C_4-saccharinic acid lactones and to erythronic lactone.
2. Both the 2,3-dihydroxybutyric acid lactone and its 2-acetylated derivative have been reduced in good yield to 3-hydroxybutyric acid lactone.
3. The 2,3-dihydroxybutyric acid lactone and the 1,3-dihydroxybutyric acid lactone showed, respectively, by analyses, 21 and 67% reduction at low pressures when large amounts of platinum oxide catalyst were used.
4. Butyl erythronate was prepared according to a modification of Snoddy's adaptation of the method of Hlasiwetz and Habermann. It was reduced to erythritol in good yield at both high and low pressures.
5. The butyl ester of 3-hydroxyisocrotonic acid and the ethyl ester of 1-hydroxy-3-chlorobutyric acid have been prepared.
6. The esters mentioned in 4 and 5 above are new to the literature.
7. Reduction of samples of the catalyst ($PtO_2 \cdot H_2O$) resulted in the production of a slight amount of alkali. This fact should not be ignored in hydrogenations of acids, esters, etc.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 8, 1937

NOTES

The Action of the Sulfonyl Group

BY F. ARNDT

In a recent paper[1] Kohler and Potter, after giving reference to a previous work of Arndt and Martius,[2] and after describing the behavior of a series of sulfonyl ketones, conclude as follows: "The view that sulfonyl groups cannot promote enolization is manifestly no longer tenable." This view, however, has not been expressed by the writer and his co-workers, who have even given detailed experimental evidence to the contrary. Thus, malonic ester does not enolize, whereas tosylmalonic ester enolizes appreciably; malonitrile does not tautomerize, but tosylmalonitrile tautomerizes considerably; acetaldehyde and tosylacetaldehyde do not enolize whereas formyl methionide, where the aldehyde group is combined with *two* sulfonyl groups in the β-position, enolizes to a great extent. On the other hand, Kohler and Potter acknowledge that "it is doubtless true that the sulfonyl group is far less effective than the carbonyl group in promoting enolization." This great difference in *degree* has been attributed by Arndt and Martius to a difference in the *nature* of the action of the sulfonyl and carbonyl groups, respectively. The action of the sulfonyl group is purely acidifying, thereby diminishing the factor which is opposed to enolization, *i. e.*, the "prototropic expenditure of work," whereas carbonyl and other groups containing multiple bonds increase, to a great extent, the active factor which promotes enolization, *i. e.*, the "electromeric effect of the molecule," by forming with the enolic double bond a conjugated system. The view that the sulfonyl group does not act in *this* manner, because it does not contain double bonds, is in no way contradicted by the experimental results of Kohler and Potter. The behavior of the group $COC_6H_2(CH_3)_3$ alone and in combination with one or two sulfonyl groups is, in fact,

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[1] E. P. Kohler and H. A. Potter, THIS JOURNAL, **58**, 2166 (1936).

[2] F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).

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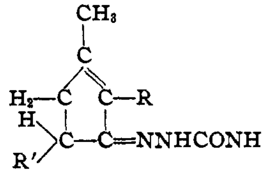
[1] H. L. Haller and F. B. LaForge, *J. Org. Chem.*, **1**, 38 (1936).

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).