On Two Stereo-Isomeric Hydrazones of Benzoin. By
Alexander Smith, B.Sc., Ph.D.

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While the theory of stereo-isomerism has been employed in the case of many carbon compounds, it has had but few applications in that of organic substances containing nitrogen. Its use has been almost confined to explaining the occurrence of isomers among the oximes. The addition of a new member to the small list of four or five pairs of hydrazones, whose isomerism can be explained only on the assumption of diversity in the disposition of the atoms in space, is therefore not unwelcome as giving additional weight to the theory.

Werner (Berichte 23, 2333) has prepared the two stereo-isomeric ketoximes of benzoin, and, in accordance with Hantsch and Werner's theory, assigns to them the formulæ :—

The two phenyl-hydrazones described below will therefore possess the formulæ :—

The following four paragraphs give briefly the reasons for believing that the substances isolated are really physical isomers.

1. When benzoin and phenyl-hydrazine, in molecular proportions, are dissolved in alcohol and warmed on the water-bath for four hours, the solution deposits on cooling, first a substance melt-

ing at 106°, and later another melting at 158–159°. They are both found to possess the composition of a monophenyl-hydrazone of benzoin, and to be identical in molecular weight. These facts, with the similarity in mode of preparation, point to identity in chemical constitution.

The lower-melting isomer may be made alone by heating the constituents together without intervention of alcohol.

2. Both substances form small white needles. The differences between them are differences in degree only. The melting-points are 52–53° apart. The lower-melting isomer here, as in previously described cases, is much more soluble in ordinary solvents than the other, and is much less stable in its general relations. Following, therefore, the established precedent, it has been designated the β -hydrazone, to distinguish it from the more stable, or α -hydrazone. The relative instability of the β variety is shown by the fact that it is rendered oily by heating in alcohol for some hours, and is soon so far decomposed that no crystals can be obtained from the solution. The α variety is unaffected by this treatment.

3. The identity in chemical constitution was proved by the conversion of both into the already known diphenyl-hydrazone of benzil, $C_6H_5 - C(N_2HC_6H_5) - C(N_2HC_6H_5) - C_6H_5$, by the action of excess of phenyl-hydrazine in acetic acid solution, and by other reactions.

4. Finally, as in the case of other isomeric hydrazones, the β modification was transformed into the α modification. This was accomplished by heating it in alcoholic solution with two molecules of phenyl-hydrazine. When we consider the instability of the β -hydrazone, the yield of .5 gram of the pure α -phenyl-hydrazone from 1 gram of the isomer indicated an unexpectedly complete transformation.

This case of stereo-isomerism is specially interesting, as in no previous case could both modifications of the hydrazone be obtained directly. One of the isomers was always obtainable only from the ketone-chloride, or by transformation from the other.