BEHAVIOR OF SOME CLOSELY RELATED COMPOUNDS WHEN MELTED TOGETHER

L. Chas. Raiford, 1917.

(Abstract)

It is a well known fact that the freezing point of a pure solvent is lowered by the presence of a non-volatile solute. This fact is utilized commercially in the preparation of low melting alloys for different uses, and in many other ways. In organic chemistry the depression of the melting point of a pure compound by admixture with foreign matter is a common behavior familiar to every worker. The depression is shown not only by mixtures of compounds that are different in composition and molecular structure, but even by such closely related substances as stereoisomers, and the question of the identity of two organic products is usually most easily decided by melting them together. On the other hand, failure to depress each other's melting point is practically always held to prove the identity of the products.

In a study of the action of halogen on 4-nitro-m-cresol, it was found by Raiford* that 2, 6-dichloro-4-amino-m-cresol, m. p. 175°, could be melted with 2, 6-dibromo-4-amino-m-cresol, m. p. 175°, with but a very slight depression (168-171°), far less than is usually observed in such cases. The structures of the two compounds show that they differ only in the replacement of chlorine by bromine. (Illustrations which cannot be printed were inserted at this point.)

This behavior made it a matter of interest to examine other compounds of similar structure, with the hope of learning if the pair cited was exceptional in this respect. Since that time four other pairs of substances have been examined, with the result that the depressions were in each case less than one degree, which would be negligible in the work of the average organic chemist. Such behavior would render it impossible to decide with certainty between two products without recourse to an analysis, and in the last case even this would not suffice, because the compounds are structural isomers. (Illustrations which cannot be printed were also inserted at this point, showing the compounds and their melting points.)

The last pair of products examined though they were obtained from a single compound, were not identical; they turned out to be structural isomers. They were carefully differentiated from each other by oxidation into their respective chlorimids, quinones, the
melting points of which were twenty six degrees apart, and in which case a very noticeable depression twenty degrees, took place when the mixture was melted. (The structures of the aminophenols and their chlorimids quinones were illustrated by diagram.)