LXX.—*The Action of Semicarbazide Hydrochloride and of 2 : 4-Dinitrophenylhydrazine Hydrochloride on Aldoximes and their Derivatives.*

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KNÖPFER (*Monatsh.*, 1910, **31**, 87) showed that the reaction

$$R\cdot CH{:}N\cdot NHPh + H_2N\cdot NH\cdot CO\cdot NH_2,HCl \rightleftharpoons R\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2 + NHPh\cdot NH_2,HCl$$

was a balanced one and that by using an excess of semicarbazide hydrochloride it was possible to convert phenylhydrazones into semicarbazones, and *vice versa.*

When an aldoxime in solution is treated at room temperature with a solution of an equivalent amount of semicarbazide hydrochloride, it is slowly converted into the semicarbazone : this, being much less soluble than the oxime, crystallises and the conversion is almost complete. It was thought possible that this replacement might lead to the production of stereoisomeric semicarbazones when stereoisomeric oximes were employed, but both the α- and the β-forms of *p*-methoxy-, *m*-nitro-, and *p*-nitro-benzaldoximes gave the same semicarbazones : search was made for small quantities of isomeric compounds, but without success. No reaction occurred when aldoximes were treated with a solution of semicarbazide itself. Apparently, therefore, the formation of the semicarbazone is preceded by hydrolysis of the oxime to the aldehyde; if this is so, the production of stereoisomeric semicarbazones would not be expected. As would be anticipated from their greater ease of hydrolysis, the *N*-methyl derivatives of the above oximes reacted more rapidly than the oximes with semicarbazide hydrochloride, giving the semicarbazones. *O*-Methylbenzaldoxime was only slowly transformed into the semicarbazone.

The following experiment typifies the method employed. A solution of α-*m*-nitrobenzaldoxime (1·6 g.) in alcohol (5 c.c.) was treated at room temperature with a solution of semicarbazide hydrochloride (1·1 g.) in water (2 c.c.). A precipitate appeared after 30 minutes, 0·7 g. of semicarbazone had separated after 12 hours, and a further 0·15 g. after 2 days. Both products were identical with *m*-nitrobenzaldehydesemicarbazone, m. p. (rapidly heated) 244°, prepared from the aldehyde. The addition of water to the mother-liquor precipitated more semicarbazone of the same melting point.

A solution of 2 : 4-dinitrophenylhydrazine hydrochloride in 2*N*-hydrochloric acid (Brady and Elsmie, *Analyst*, 1926, 77) reacts somewhat readily at room temperature with aldoximes and their derivatives, giving practically quantitative yields of the crystalline 2 : 4-dinitrophenylhydrazones of the corresponding aldehydes. Owing to the sparing solubility and non-volatility of these compounds the reaction provides a method for the quantitative determination of small quantities of oximes.

The following experiments indicate the scope of the method. (1) *α*-*p*-Nitrobenzaldoxime (0·1707 g.) was dissolved in alcohol (5 c.c.) and to this was added a solution of 2 : 4-dinitrophenylhydrazine hydrochloride (250 c.c.) in 2*N*-hydrochloric acid containing 1 g. of base per litre. The mixture was kept with occasional shaking for 24 hours and the precipitated *p*-nitrobenzaldehydedinitrophenylhydrazone was then collected in a Gooch crucible, washed with 2*N*-hydrochloric acid and with water, and dried at 100° to constant weight. The yield of dinitrophenylhydrazone (0·3194 g.) corresponded to 93·5% of the oxime taken. (2) Similarly, *N*-methyl-*o*-methoxybenzaldoxime (0·1055 g.) in water (10 c.c.) gave dinitrophenylhydrazone (0·2018 g.) corresponding to 99·9% of the compound taken. (3) A saturated aqueous solution of *o*-methoxybenzaldoxime at 18° was found by this method to contain 0·868 g. per litre. A direct determination by extraction with ether and weighing gave 0·880 g.

Although *O*-methylbenzaldoxime can be hydrolysed only with difficulty by acids and is unusually unreactive, yet on shaking with a solution of 2 : 4-dinitrophenylhydrazine hydrochloride and keeping for 2 days it is quantitatively converted into benzaldehydedinitrophenylhydrazone, from which benzaldehyde can be obtained by warming with moderately concentrated sulphuric acid. This is the easiest method of recovering the aldehyde from the *O*-methyl derivative of the oxime.

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