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<tr>
<td>Author(s)</td>
<td>Oda, Ryohei; Nakano, Kazuhiro; Isoda, Makio</td>
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<tr>
<td>Citation</td>
<td>京都大学化学研究所報告 (1950), 20: 62-63</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1950-03-20</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/74046">http://hdl.handle.net/2433/74046</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>Publisher</td>
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We could not succeed to obtain the reaction-product from \(~\text{w-nitrostyrol}\) and diazonium salts:

27. A New Method to Replace the Diazonium-Salt Group with Halogen.

Ryohei Oda, Kazuhiro Nakano and Makio Isoda.

Generally, the replacement of diazonium-salt group by halogen takes place in the presence of a cuprous salt (Sandmeyer) or copper powder (Gattermann).

We have discovered a new method of the replacement for the same purpose, as follows.

When the double salt of diazonium salt and zinc chloride is heated in such a suitable solvent as ether, benzene or toluene, the diazonium-salt group is replaced by a chlorine atom in good result.

Preparation of the double salt:

Aromatic amine is dissolved in hydrochloric acid solution and diazotised with sodium nitrite solution. After filtering, zinc chloride is added and then sodium chloride. The crystalline diazo-compound is collected, pressed and dried.

Reaction of the replacement:

To some suitable solvent contained in a round-bottomed flask with a reflux condenser is added the double salt. In this case the diazonium compound is insoluble in the solvent. And then warm the flask content gradually on a water bath with good shaking and the double salt begins to decompose with the evolution of nitrogen and goes into a clear solution. When the decomposition reaction is at an end, wash the reaction mixture with water and distil the layer of the solvent. According to this method, the diazonium salt is not hydrolyzed to the hydroxy compound, but the corresponding chloride is got as a reaction product with good yield.

We describe the results of our experiments hereunder.

In ether at 35°C for 5 hrs.

From benzene-diazoniumchloride, \(~\text{m-}, \text{o-} \text{toluene-diazoniumchloride}\).

Chlorbenzen 79% \(~\text{m-} \text{chlorotoluene} \text{85%} \text{ o-chlorotoluene} \text{84%}\)

In benzene at 80°C for 5 hrs.

From \(~\text{p-toluene-diazoniumchloride}, \text{m-}, \text{p-} \text{chlorbenzenediazoniumchloride}, \text{p-} \text{nitrobenzene-diazoniumchloride}\).

\(~\text{p-chlorotoluene} \text{75% m-} \text{dichlorbenzene} \text{70%} \)

\(~\text{p-dichlorbenzene} \text{36%} \text{ p-chloronitrobenzene} \text{35%}\)

In toluene at 100°C for 5 hrs.

From \(~\text{p-chlorbenzene-diazoniumchloride} \text{ p-}, \text{m-}, \text{o-} \text{nitrobenzene-diazoniumchloride}, \text{p-}, \text{o-} \text{anisoldiazoniumchloride}\).
28. Physico-Chemical Studies of the Polymerization of Rice Oil.

Itsuro Yamakita and Sadatoshi Tomioka.

The studies on the polymerization of rice oil performed up to date is, in general, that of low acid value (below 46.5). So the authors set to work on higher acid value oil, most frequently met with in the practical case, in order to find the way of utilizing it most effectively from the economical standpoint.

In our experiments, a winter rice oil (acid value, saponification value and iodine value being 106.0, 182.0, and 108.6 respectively) was used. The polymerization procedure was carried out at 300°C in hydrogen atmosphere and the change of viscosity, mean molecular weight, and iodine value of the sample were measured. The results are formulated as follow:

1) The relation between viscosity increased and concentration of the polymerized oil in benzene solution, measured at 25°C, is given by the equation: \[ \eta_{sp} = k_0 C_v + k_1 C_v^2 \]

where \( C_v \) is grams of the solute in 100 cc. benzene solution, \( \eta_{sp} \) is the specific viscosity, \( k_0 \) and \( k_1 \) are constants. \( k_0 \) is calculated in particular from the value of \( \eta_{sp}/C_v \) at \( C_v \to 0 \), called "intrinsic viscosity" and independent of the concentration of solution, (\( k_0 \) will be used conveniently in stead of \( \eta_{sp} \) hereafter).

2) The relation between the change magnitude of \( k_0 \) increase, \( K \) say, and that of iodine value decrease by the polymerization progress, is given by the equation: \[ \log (K-C) = b \log I + a, \]

where \( a, b, \) and \( c \) are constants.

3) The relation between \( K \) and the magnitude of increase of mean molecular weight, \( M \), determined by Rast’s camphor method at the corresponding polymerization stage, is given by the equation: \[ K = 3.44 \times 10^{-3} M. \]

4) The rate of the change of \( K \) value to the time of polymerization, \( t \), is given...