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REDUCTIVE COUPLING OF OLEFINIC COMPOUNDS BY AN ALKALI METAL AMALGAM

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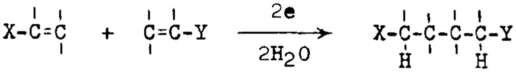
Knunyants and Vyazankin (1-2) reported hydrodimerization by alkali metal amalgams of a number of derivatives of α,β-unsaturated acids in acidic medium. The yields of the hydrodimers were relatively low.

Baizer (3-14) has observed and studied the electrolytic reductive coupling of olefinic compounds in electrolytes containing quarternary ammonium arylsulfonates. In these experiments the yield of the coupled products was quantitative. The equation (7) for the reductive coupling is



$$X-\overset{|}{C}=\underset{|}{\overset{|}{C}} + \underset{|}{\overset{|}{C}}=\overset{|}{C}-Y \xrightarrow[2H_2O]{2e} X-\underset{H}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-Y$$

X, Y = $-CN$, $-COOR$, $-CONR_2$, etc.

Our laboratory has developed a high yield process using alkali metal amalgams in the presence of catalysts for the non-electrolytic reductive coupling of α,β-monoolefinic nitriles, carboxylates, amides and ketones.

It was found that high yields of the hydrodimers could be obtained at pH's of 2 to 12 in the absence of an external electrolytic circuit when certain catalysts were added to the reaction medium. It was also found that under the same experimental conditions coupling of two unlike olefinic compounds could be obtained. It thus furnishes a method not only for obtaining hydrodimers in high yield but also for preparing a variety of polyfunctional compounds.

When a mixture of two different olefins is employed, three different products are usually obtained: two different hydrodimers by self coupling and the product of mixed coupling. For example, the reductive coupling reaction of a mixture of acrylonitrile and ethyl acrylate yielded 6.5% adiponitrile, 13.2% diethyl adipate and 80.3% ethyl δ-cyanovalerate.

The catalysts used in this process were urea and its derivatives, amides, lactams, sulfoxides, sulfones and quarternary ammonium salts, such as 1,3-dimethylurea, ethylene urea, biuret, formamide, N-methylformamide, acetamide, γ-butyrolactam, dimethyl sulfoxide, di-n-butyl sulfoxide, dimethyl sulfone, tetramethylammonium halides, tetraethylammonium halides, tetraethylammonium p-toluenesulfonate, etc.

A solvent used for dissolving monomers in most experiments was N,N-dimethylformamide which was found not to be used as a catalyst for the reductive coupling. However, 1,3-dimethylurea, N-methylformamide, γ-butyrolactam, dimethyl sulfoxide and tetraethylammonium p-toluenesulfonate were found to be used not only as the catalysts but also as the solvents.

The yield of the coupled products of olefins was high whether one calculated the yield on the basis of olefin used or sodium used. The following may serve as an example for the formation of reduced coupled products by this procedure.

A solution was prepared containing 35.3 g. of acrylonitrile with a trace of p-methoxy phenol, 9.0 g. of water and 70.3 g. of 1,3-dimethylurea. This solution was added into a 500 ml. four necked flask containing 50 ml. of mercury.

A 210.0 g. of electrolytically prepared sodium amalgam containing 0.511% by weight of sodium was dripped into the flask over a period of 15 minutes.

The solution in the flask was saturated with carbon dioxide to maintain the pH of the solution at 8 to 10 during the reaction. The temperature of the solution was kept at 25°C to 30°C.

At the end of the reaction, the solution was diluted with water, extracted with dichloromethane and dried over potassium carbonate. The dried product was evaporated to obtain the substantially pure adiponitrile.

Analysis of the dried product by gas chromatography showed that 3.08 g. of adiponitrile and 0.12 g. of propionitrile were obtained. The yield of adiponitrile calculated on the basis of the acrylonitrile used was 96.2%, while the yield calculated on the basis of the sodium used was 84.3%.

It was observed that the yield of adiponitrile increased with increasing the concentration of 1,3-dimethylurea in the solution passing through a maximum when the ratio of 1,3-dimethylurea to acrylonitrile was approximately 1:1 and then decreased at higher concentration of 1,3-dimethylurea.

Although Knunyants (1) proposed a free radical mechanism, our results are best interpreted by the following ionic mechanism. The α,β-olefinic compound can be assumed to form a polarized adduct with the catalyst. The formation of this adduct makes it easier for the olefin to take two electrons at the β-position to form a dianion such as $(CH_2CHCN)^{-2}$ proposed by Baizer (10). It was also found that the yield of adiponitrile was not affected by the addition of a radical absorber such as p-methoxy phenol. This ionic mechanism might easily explain the high selectivity for the hydrodimerization and the high yields of the hydrodimers. So far the studies have not established the nature of the adducts of olefins and catalysts.

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