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COMMERCIAL METHODS OF SYNTHESIS OF α,β-UNSATURATED ALDEHYDES AND KETONES

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I. INTRODUCTION

α,β-Unsaturated aldehydes of the acrolein series and ketones are of great interest as starting materials for the production of polymers and copolymers with an active functional (carbonyl) group; they can also be used to obtain other monomers and many other products.

Acrolein has already become an important commercial material. Industrial methods have been developed for the production from it of allyl alcohol[1-4], glycerol[5-7] and its derivatives[8], and acrylonitrile[9-11]. The chemistry of acrolein has recently been attracting great attention[12-20]. In the Federal Republic of Germany intense work is going on on the polymerisation products of acrolein itself[21,22]. Furthermore, even now a considerable quantity of acrolein is used for the production of methionine, a substance which accelerates the growth of poultry when added to their feed[23]. In the U. S. A. the Carbide Chemical Corporation has constructed a plant for the production of a number of acrolein derivatives on an industrial scale[24,25].

Methacrolein has not yet found wide use as a commercial intermediate because it is much less readily available, but potentially it is of interest for chemical synthesis. According to the literature[26-30] methacrolein is readily converted into substances of value to the plastics industry, such as methacrylic acid, methylallyl alcohol, and polyhydric alcohols.

α,β-Unsaturated ketones have also not yet taken on great industrial significance, apparently mainly because of their relatively low availability. There are reports[31] of the preparation from polyvinylketones of lacquers, unbreakable glass, plastics, and so on. Colourless monomers produce crystally pure polymers of remarkable optical properties[32]. Many copolymers of methyl vinyl ketone[33-35], isopropenyl methyl ketone[36-44], and phenyl vinyl ketone[45,46] have been described. There are indications[47] that after treatment with phosphoric acid copolymers of styrene with methyl vinyl ketone or isopropenyl methyl ketone are extremely resistant to heat and withstand the action of a

flame. Rubbers prepared by the emulsion copolymerisation of isopropenyl methyl ketone with divinyl are better than divinylstyrene rubbers in some of their properties[48].

II. SYNTHESES OF α,β-UNSATURATED ALDEHYDES OF THE ACROLEIN SERIES

There were no commercially acceptable methods for the production of acrolein until the 1940's, when the German firm of Degussa developed an industrial method for its production by the aldol condensation of formaldehyde with acetaldehyde[49].

In the United States in 1946–1948 the Shell Chemical Corporation developed a commercial method for the synthesis of acrolein by the pyrolysis of diallyl ether[50], which is a by-product in the preparation of allyl alcohol from allyl chloride[51]. Acrolein has been obtained by this method in a plant of capacity ~9 tons per month[50]. The pyrolysis is carried out at 520° and 2.1 atm.; the yield of acrolein based on reacted ether was 86% at a conversion of ether of 90% per pass. This method has no commercial significance at present, because it is more economical to prepare allyl alcohol from acrolein.

The possibilities of the industrial utilisation of acrolein increased significantly when acrolein was shown to be obtainable in high yield by the oxidation of propene. At present this is considered the most promising method for the synthesis of acrolein.

Methods for the production of methacrolein have also been improved. A patent[52] describes the production of methacrolein in 57–60% yield by the pyrolysis at 500–570° of di-2-methylallyl ether, which is a by-product in the preparation of methylallyl alcohol by the alkaline hydrolysis of 3-chloro-2-methylprop-1-ene.[53]

Methods are now being developed for the production of methacrolein by the aldol condensation of formaldehyde with propionaldehyde and by the oxidation of isobutene.

The preparation of methacrolein and other α-alkylacroleins by the Mannich reaction has recently been shown to be commercially feasible.

At present there are thus several convenient methods for the production of α,β-unsaturated aldehydes of the acrolein series. Depending on the actual circumstances, the following are commercially feasible: the oxidation of alkenes, the aldol condensation, and the method based on the Mannich reaction, and these are considered in more detail below.

1. Production of α,β-Unsaturated Aldehydes by the Direct Oxidation of Alkenes

As already stated, the direct oxidation of propene is considered abroad as the most promising method for the production of acrolein:

$$CH_2{=}CH{-}CH_3{+}O_2 \xrightarrow{200-450^\circ} CH_2{=}CH{-}CHO{+}H_2O\,.$$

Similarly isobutene can be oxidised to methacrolein:

$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3{+}O_2 \longrightarrow CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CHO{+}H_2O\,.$$

In 1950 the Shell Chemical Corporation set up a test plant for the catalytic oxidation of propene to acrolein of capacity 2 tons per month[54], and at the end of 1959 it opened a factory for the production of glycerol from acrolein; this is still the largest works in the world for the production of acrolein, its annual capacity being estimated at 13 620 tons of acrolein[22]. A similar process has been developed and taken to the pilot plant stage by the Italian firm of Montecatini[55-58].

The literature on this method is mainly concentrated in patents, and only in recent years have these processes attracted any considerable attention from Soviet chemists, who have published a good deal of work on the choice of catalysts and the influence of various factors on the process[59-91].

The reaction is conducted at 200–450° and pressure close to atmospheric[22,92-94]. The propene : oxygen ratio varies, according to different sources, from 2 : 1 to 30 : 1, the lower ratios being most often used. Air or a mixture of oxygen with carbon dioxide or steam is employed as oxidant. Paraffinic hydrocarbons are inert under these conditions and do not interfere in the process[95]; some patents even recommend their use as diluents[96].

Several types of catalyst have been described for the oxidation of alkenes: copper(I) oxide on a carrier[22]; copper(II) oxide on a carrier in the presence of selenium[22]; mixtures of various metals of variable valency or their oxides[97-105]; metal selenites or tellurites promoted by various oxides[106-108]; and molybdates, chromates, sulphates, molybdophosphates, vanadates, aluminates, and silicates of various metals (copper, bismuth, cobalt, and others)[59,109-114]. Copper(I) oxide is the most used[22].

As carriers there are used silicon carbide[22], ceramically combined compositions of aluminium and silicon[115], pumice[64], alumina[22], and others. The process can be successfully worked on a catalyst without any special carrier[57,58].

The main side reaction in the oxidation of propene to acrolein is the formation of carbon dioxide and water; considerable amounts of formaldehyde and acetaldehyde are also produced, as well as carbon monoxide, organic acids, various carbonyl compounds, and relatively small amounts of polymers, which can deactivate the catalyst.

The catalyst requires periodic regeneration. The reduced activity is manifested in two ways, a lessened selectivity and a lessened productivity, the former because of change in the composition of the catalyst, and the latter because of deactivation of the active centres by catalytic poisons or polymers[22]. Regeneration is therefore carried out in two ways: by changing the working conditions (reactant ratios and temperatures), which changes the chemical composition of the catalyst[116,117], and by burning off the deposits at a higher temperature (400–500°).[118]

Considerably improved yields of the unsaturated aldehydes are obtained by using halogens as promoters, added as such or as organic halogen compounds. Addition of 0.02 vol. % halogen derivative to the total reactant gas mixture increases the selectivity by 5–10% and the productivity of the catalyst by 30%.[87] Addition of iodine[119-121] has substantially increased the life of the catalyst, and has given a conversion of propene of 78–82% per pass with a 70–79% yield of acrolein. Without the halogen a greater selectivity requires a lower conversion per pass; according to the data available, the conversion of propene per pass should not then exceed 10–25%.[92-94]

Addition of selenium to copper catalysts considerably increases the selectivity and productivity of the catalyst.

According to Kruzhalov *et al.*[85], the selenium acts by blocking, by chemisorption, the active centres which catalyse the complete oxidation of the propene, while in the formation of acrolein it participates in the transfer of oxygen to the propene molecule. When using selenium the yield of acrolein reaches 81–82% with a propene conversion of 90–95% per pass. The recommended selenium concentration is 0.008–0.12 mg per litre of gas mixture[122]. Thus by using selenium the alkene need not be recycled, but because of its high toxicity it must be almost completely removed from the reaction gases, for example, by passing them through active carbon[123]. In recent years sulphur has been recommended instead of selenium, since this also increases the activity and life of the catalyst, but is not toxic[124].

As already stated, under analogous conditions isobutylene is oxidised to methacrolein; yields of 73–78% with an isobutene conversion of up to 33% are attained[84,124-133].

The oxidation of alkenes gives a complex mixture of products, and the separation of the reaction products and isolation of the pure unsaturated aldehydes is one of the main problems in the commercial operation of the process, and special methods have to be employed. Many patents have been devoted to this problem; the most important are referred to in Sherwood's reviews[22,92-94].

The production of unsaturated aldehydes by the oxidation of alkenes is very promising for large-scale production, since a cheap starting material is used. A substantial disadvantage of this method is the considerable technological difficulties involved in the industrial working of the process, especially in the separation of the reaction products.

2. Production of α,β-Unsaturated Aldehydes by the Aldol Condensation of Formaldehyde with Aliphatic Aldehydes

In 1950 Schulz and Wagner published the results of their investigations[49], which led to the development of the first industrial synthesis of acrolein by the aldol condensation of formaldehyde with acetaldehyde. In Germany in 1940 this method was taken to the pilot plant stage with a capacity of 1 ton of acrolein per month[49], and now there is a semi-industrial plant with a capacity of 10–20 tons per month[134]. Acrolein has been obtained by this method in the United States since 1955 by the Carbide and Carbon Chemical Corportion[135].

The reaction takes the course:

$$HCHO+CH_3CHO \rightarrow CH_2OHCH_2CHO \rightarrow CH_2{=}CH{-}CHO+H_2O.$$

In Germany the process is carried out in the vapour phase at 280–330° over silica gel of large pore size containing 10% sodium silicate[134], the latter reducing the formation of resins. Pure silica gel is extremely active, but even after 1 h its activity is completely lost because of almost complete resinification. When impregnated with sodium silicate the catalyst works for 150 h without marked diminution of activity, after which it can be regenerated by oxidation of 500–550° in a stream of water vapour and air.

Catalysts which have been recommended are magnesium silicate, calcium phosphate, aluminium phosphate, and alumina[49], also oxides of zinc, thorium, and titanium[136], and lead acetates and chromates[137].

At 300–325° and a contact time of 7–8 s, the yield of acrolein, based on reacted material, is 72–75% on the formaldehyde and 79–82% on the acetaldehyde (after losses during the separation) with an average conversion per pass of 50–52% for formaldehyde and 44–46% for acetaldehyde[49].

By-products of the reaction are crotonaldehyde (up to 10%), methyl formate (up to 3%), methanol (~6%), formic acid (3%), and small amounts of a gas consisting of CO, CO_2, and alkenes.

The yields obtained by the German workers have been confirmed by Dabagov *et al.*[138] Broad studies of this synthesis of acrolein have been conducted by Malinowski and coworkers[139-145], and it has attracted considerable attention in Japan[146-148].

The reaction products are separated by a relatively simple industrial rectification process[135]. An azeotropic mixture of acrolein and water (2.7–3.0% water) is obtained; when treated with 0.1% hydroquinone or other inhibitor it can be stored for several years.

The production of methacrolein by the aldol condensation of formaldehyde with propionaldehyde can be carried out in the vapour or liquid phase. The vapour-phase process is analogous to that for acrolein, and the same catalysts and reaction conditions can be used[137,149-151]. Thus one of the patents[151] indicates that methacrolein can be obtained in almost quantitative yield by carrying out the condensation at 300–320° over a catalyst comprising activated silica gel of large pore size impregnated with alkali metal phosphates or silicates. However, according to Malinowski[141-149] the yields of methacrolein in the vapour-phase condensation do not exceed 40–59%.

The liquid-phase process also uses various catalysts. Methacrolein has been obtained in 84.5% yield by carrying out the condensation at 100° in the presence of $BF_3.H_2O$;[125,152] the conversion of propionaldehyde was 24.9%. A patent[153] describes the production of methacrolein in high yield at 20–30° in the presence of sodium carbonate.

The aldol condensation of formaldehyde with other aldehydes having at least two hydrogen atoms on the carbon atom in the alpha position to the carbonyl group gives higher α-alkylacroleins in yields of up to 59%.[141,149,151]

The production of α,β-unsaturated aldehydes by the aldol condensation of formaldehyde with aliphatic aldehydes therefore has a definite technological value because it is simpler to realise industrially than the oxidation process, although it uses more costly starting materials.

3. Production of α,β-Unsaturated Aldehydes by the Mannich Reaction between Formaldehyde and Aldehydes

The wide possibilities in the choice of reagents, diversity of choice for the subsequent conversion of the Mannich bases, and the mild reaction conditions of the Mannich reaction have made it an important process in modern organic chemistry[154,155].

Investigators of the Mannich reaction were able to show a relatively long time ago that it can provide unsaturated compounds, including carbonyl monomers. However, for a long time this reaction had no technological value, apparently mainly because of its poor reproducibility. Mannich *et al.*[156] were the first to show the possibility of obtaining α,β-unsaturated aldehydes by this route.

This process (for example, for the production of methacrolein) is based on the reactions:

$$CH_3CH_2CHO+CH_2O+R_2NH\cdot HCl \longrightarrow \underset{\underset{CH_2NR_2\cdot HCl}{|}}{CH_3CHCHO} + H_2O,$$

hydrochloride of Mannich base

$$CH_3CHCHO \longrightarrow CH_2=\underset{|}{C}(CH_3)-CHO+R_2NH\cdot HCl.$$

For the production of unsaturated carbonyl compounds the Mannich reaction is best carried out with salts of secondary amines. The use of ammonia or primary amines always leads to undesirable reactions, since the resulting Mannich bases, being primary or secondary amines, can themselves produce various by-products [157-159].

Beginning in 1939, a series of patents [160-164] and communications [165-167] appeared on the production of α,β-unsaturated aldehydes by this method. A main disadvantage of the method, which hindered its wide application, was that the yields of the unsaturated aldehydes varied, according to the data obtained by various workers, over very wide limits [160,161,163,164,166,167], with reaction times of from 6 to 24 h. [165,166] As a rule these syntheses had been carried out under conditions far removed from optimum, and had not been investigated from the point of view of the conditions necessary to ensure a high yield of the desired products.

The detailed investigations of Farberov and his coworkers [168-173] have enabled the irreproducibility of the Mannich reaction to be circumvented and have allowed the process to be taken to the stage of industrial realisation. As exemplified in the production of methacrolein, the rate of the Mannich reaction with aliphatic aldehydes was shown to be very strongly dependent on the pH of the medium. At pH 3-4, which is the usual range when the reagents are mixed in equimolar proportions, the reaction proceeds at a satisfactory rate only 100-120°, where there is a considerable polymerisation of the resulting unsaturated aldehyde. Adjusting the pH to 6-7 greatly accelerates the reaction and enables it to be conducted at relatively moderate temperature, and a nearly quantitative yield can be obtained. At pH 7 and 45° quantitative conversion is attained in 20-30 min. Heating the reaction products (without preliminary separation of the Mannich base) gives quantitative separation of methacrolein as an azeotrope with water. Pure methacrolein is readily obtained by azeotropic drying. The resulting amine salt solution can be recycled to the process after concentration. The synthesis of methacrolein (yield 98.7% of theory), α-ethylacrolein (97.9%), and α-isopropylacrolein (90%) is described. The methacrolein synthesis has been tested on a semi-industrial plant; a continuous process for its production has been developed in principle.

It is thus seen that the Mannich reaction can be used to obtain α,β-unsaturated aldehydes in yields close to theoretical, under very mild conditions and in very simple apparatus. The process requires more costly starting materials than the alkene oxidation process, but the practically quantitative conversion of the initial aldehydes per pass, the quantitative yields of α,β-unsaturated aldehydes, and the extremely simple apparatus, together with the complete absence of side reactions, make this process very profitable.

Another advantage of this method is the possibility of preparing a whole series of α,β-unsaturated aldehydes. The preparation of the following has been described: methacrolein [160-164,166,167], α-ethylacrolein [160-163,166,167], α-isopropylacrolein [165-167], α-propylacrolein [166,167], α-butylacrolein [166,167], α-t-butylacrolein [166], α-pentylacrolein [165], and α-phenylacrolein [162].

Recently Farberov and coworkers [174] have shown that this method can provide the previously unobtainable 2,4-dienals in high yields, so broadening the range of application of the Mannich reaction for the production of unsaturated aldehydes.

III. SYNTHESES OF α,β-UNSATURATED KETONES

α,β-Unsaturated ketones have long attracted the attention of investigators. Berlin's review of the methods of production of vinyl ketones [175] appeared as early as 1939. At present there are several commercially valuable methods for the production of α,β-unsaturated ketones.

1. Production of α,β-Unsaturated Ketones by Hydration of Vinylacetylenes

This method is of commercial interest mainly for the synthesis of methyl vinyl ketone.

The hydration of vinylacetylene to methyl vinyl ketone was first achieved by Nieuwland [176,177] and was subsequently studied in detail by Churbakov and Ryazantsev [178,179].

$$CH_2=CH-C\equiv CH+H_2O \rightarrow CH_2=CH-COCH_3.$$

The hydration is carried out in an acid medium in the presence of mercury salts (generally the sulphate) at a temperature not above 70-80°. [178,179] To prevent reduction of the mercury(II) to inactive mercury(I) an oxidising agent, such as iron(III) sulphate, is added to the reaction mixture to convert the mercury(I) salt into the active mercury(II) salt [178]. The yield of methyl vinyl ketone reaches 90% on reacted and 77% on taken vinylacetylene [178-180]. The patent literature describes apparatus for the continuous production of methyl vinyl ketone by this method [180-182]. Some patents recommend complete hydration of the vinylacetylene to acetoin in the presence of mercury(II) sulphate, with subsequent dehydration to methyl vinyl ketone [183,184]. The main disadvantage of this method is the use of toxic mercury compounds.

A relatively recent communication [185,186] reported the hydration of vinylacetylene in the vapour phase over catalysts not containing mercury: cadmium tungstate, cadmium calcium phosphate, tungsten trioxide, and zinc oxide; the first two show the greatest selectivity in respect of yield of methyl vinyl ketone. The reaction was effected at 325-400°. The yield of methyl vinyl ketone reached 87% on reacted vinylacetylene, with a 31.8% conversion. By-products obtained were methyl vinyl ketone dimer (3-4%) and a polymer of vinylacetylene (1-1.5%).

Hydration of isopropenylacetylene produces isopropenyl methyl ketone in a yield of up to 91%, [187-190] but because of the poor availability of the starting isopropenylacetylene this method has no commercial value.

The process is thus of commercial value only for the production of methyl vinyl ketone.

2. Production of α,β-Unsaturated Ketones by the Aldol Condensation of Formaldehyde with Saturated Ketones

This method is analogous to the corresponding method for the production of α,β-unsaturated aldehydes, and can similarly be carried out in vapour or liquid phase.

The vapour-phase condensation is conducted at 250–450° in the presence of catalysts: lead zeolite catalysts[191]; silica gel[149,192]; silica gel impregnated with a 1% solution of NaOH, KOH, or RbOH[149,192]; alumina containing oxides of zirconium, cerium, thorium, zinc, or magnesium[193]; industrial KDS catalyst [catalyst used in synthetic rubber production(Ed. of Translation)][194]; Cd, Ca phosphate[194]; rare-earth oxides[194]; and various natural clays[194]. The reactant ratios employed vary, according to different sources of data, from equimolar[194] to a four-fold excess of acetone[191]. This method has produced the following ketones, in the yields indicated: methyl vinyl ketone (40–99%)[191,192,194], isopropenyl methyl ketone (28–97%)[191,192], 1-isopropylvinyl methyl ketone (86.6%)[191], 1-ethylvinyl methyl ketone (22.6%)[192], and phenyl vinyl ketone (77.5%)[191] as well as others.

The main disadvantage of this method is that the resulting vinyl ketones are contaminated with formaldehyde and various by-products, such as hydrocarbons, alcohols, and resins. Moreover, the vinyl ketones obtained by the vapour-phase process give, on polymerisation, unstable and irreproducible results; often coloured gels with various inclusions are obtained, instead of colourless transparent solid polymers. This has been shown to be due to the presence of impurities which are difficult to remove[190].

The liquid-phase condensation is of much greater value, and has been used for the production of isopropenyl methyl ketone on an industrial scale[31].

The aldol condensation of formaldehyde with acetone:

$$CH_3COCH_3+CH_2O \rightarrow CH_3COCH_2CH_2OH \xrightarrow{-H_2O} CH_3COCH{=}CH_2.$$

takes place at pH 8.5–9.5 in an aqueous or alcoholic medium. The total yield of methyl vinyl ketone obtained in aqueous medium is 10–18%.[195-198] Higher yields (up to 50% of theory) may be obtained in an aqueous medium with a higher ratio of acetone to formaldehyde (up to 30 : 1)[199,200]. The catalyst is sodium hydroxide, in amount not exceeding 0.5–0.8 wt. % of the reaction mixture; the use of more sodium hydroxide produces a yellow viscous mass insoluble in water[32]. Recent studies of the influence of the reaction conditions on the aldol condensation of acetone with formaldehyde[201-203] indicate that the optimum yield of 1-hydroxybutan-3-one, and hence of methyl vinyl ketone (up to 65% of theory), is obtained by using a fourfold excess of acetone at 40–45° in an alcoholic medium.

The aldol condensation of formaldehyde with acetone is a very complex reaction, and the nature of the final products depends on the reactant ratio employed. By-products obtained are 4-hydroxy-4-methylpentan-2-one (4–5%), 2-hydroxybut-1-en-3-one (14–15%), 1,3-dioxan-5-yl methyl ketone (3–4%), and 1,3-dioxan-5-yl isobutenyl ketone (10–11%)[196], and also resinous high-molecular polymers of the enol form of the hydroxybutanone[131].

Because of the large amounts of by-products and the low yields of methyl vinyl ketone, this method has no commercial value.

Isopropenyl methyl ketone is obtained more smoothly:

$$CH_3COCH_2CH_3+CH_2O \xrightarrow{NaOH} CH_3COCH(CH_2OH)CH_3 \xrightarrow[-H_2O]{} CH_2{=}\overset{\displaystyle CH_3}{\underset{|}{C}}{-}COCH_3+H_2O.$$

This reaction was investigated by Staudinger and Ritzenhalter[204] and later by Morgan *et al.*[32]; the latter found excess of formaldehyde to be as harmful in the reaction with ethyl methyl ketone as in the reaction with acetone.

Best yields of isopropenyl methyl ketone are obtained by using the reagents in the proportions 11 moles ethyl methyl ketone, 10 moles formaldehyde, and 0.02 mole NaOH. The reaction mixture is initially heated to 50–60°, and then because of the exothermic nature of the reaction it is cooled to 20–25°. During the condensation the formaldehyde can undergo the Cannizaro reaction under the influence of the alkali, and so it is necessary to continue adding alkali to maintain the pH of the medium constant. The yield of 1-hydroxy-2 methylbutan-3-one is 82.7% and 42% on reacted ethyl methyl ketone and formaldehyde respectively.

The resulting 1-hydroxy-2-methylbutan-3-one is readily dehydrated to isopropenyl methyl ketone by distillation in the presence of oxalic acid[31,205]. Other dehydrating agents (iodine, potassium hydrogen sulphate, zinc chloride, etc.) are not recommended for extensive use, since they reduce the optical quality of the polymerisation product[31]. The yield of isopropenyl methyl ketone is ~80%, based on the hydroxybutanone; the optimum overall yield of isopropenyl methyl ketone is thus ~66% based on ethyl methyl ketone, and ~33% based on formaldehyde. The yield of isopropenyl methyl ketone based on formaldehyde has since been considerably improved (to 55%)[206]. Conditions have been found[37-39] for obtaining the hydroxybutanone in 87% yield, and according to a patent[205] this can be decomposed to give a 95% yield of isopropenyl methyl ketone.

It has recently been recommended[207,208] to carry out the condensation in the presence of triethylamine (pH of the mixture 10.8–11.0) with a ratio of ethyl methyl ketone to formaldehyde of 30 : 1; at 80° and a pressure of 3.2 at [1 at = 0.968 atm (Ed. of Translation)], reaction is complete in 16 min. The dehydration is accomplished in the presence of 5% aqueous phosphoric acid in a distillation column. The isopropenyl methyl ketone is obtained in a yield of up to 86.6% of theoretical, together with ethyl vinyl ketone (less than 8%) and traces of isopropenyl vinyl ketone.

Attempts to condense formaldehyde with aliphatic aromatic ketones in the liquid phase in the presence of alkaline or acid catalysts have been unsuccessful[175], but relatively recently it was reported[209] that phenyl 1-phenylvinyl ketone is obtained in 75% yield by the reaction of benzyl phenyl ketone with excess of paraformaldehyde in the presence of alkali.

The liquid-phase aldol condensation at present is seen to have a certain commercial value only for the production of isopropenyl methyl ketone.

3. Production of α,β-Unsaturated Ketones by the Mannich Reaction between Formaldehyde and Saturated Ketones

Even Mannich himself[210,211] indicated the possibility of obtaining α,β-unsaturated ketones by reacting formaldehyde, a secondary amine hydrochloride and saturated

ketones to produce hydrochlorides of Mannich bases followed by decomposition to the vinyl ketone and the secondary amine hydrochloride. With methyl vinyl ketone the reactions are:

$$CH_3COCH_3+CH_2O+R_2NH \cdot HCl \longrightarrow CH_3COCH_2CH_2NR_2 \cdot HCl+H_2O,$$
$$CH_3COCH_2CH_2NR_2 \cdot HCl \longrightarrow CH_3COCH=CH_2+R_2NH \cdot HCl.$$

There have since been several papers [158,212-221] and a patent [222] on the production of α,β-unsaturated ketones by this method. The main disadvantage of the process until now, as in the production of α,β-unsaturated aldehydes, has been the poor reproducibility of the Mannich reaction, which has prevented wide application of the method even for preparative purposes. For instance, in 1949 Hagemeyer [214] reported the production of methyl vinyl ketone and isopropenyl methyl ketone in yields of 80.5% and 81.9% respectively. Subsequently some workers [215,216] have confirmed Hagemeyer's yields, while others [223,224] have obtained low yields of the vinyl ketones. Clearly the reaction conditions suggested by Hagemeyer do not ensure a reproducible process.

This deficiency has been made good by Farberov and coworkers [171-173,225,226], who have made this process commercially feasible. Their detailed study of the Mannich reaction with a number of ketones has ensured complete reproducibility of experiments and a high rate of reaction, so that α,β-unsaturated ketones can be obtained in high yields (82-95%) and in a relatively short time. As already stated, in the synthesis of methacrolein and other α-substituted acroleins by the Mannich reaction the pH of the reaction mixture has an exceptional influence on the rate of reaction, the latter being satisfactory only at pH 6-7. The pH of the reaction mixture is of even greater importance in the production of α,β-unsaturated ketones, since it affects not only the rate of the Mannich reaction, but also the yield of the Mannich base reaction products, and consequently the yield of α,β-unsaturated ketones. The Mannich reaction with ketones proceeds at a satisfactory rate only at low pH values; at pH 6-7 (the optimum range for the production of methacrolein) a Mannich base is not formed. At 100° and pH 1 there is quantitative conversion of the starting materials in 1.5-2.0 h.

In our opinion [171,172] this dependence of the rate of aminomethylation on the pH of the medium indicates that the reaction proceeds by several different mechanisms. The Mannich reaction with aldehydes, which is accelerated by increase of pH, apparently proceeds by a nucleophilic substitution mechanism (S_N2) with intermediate formation of a carbanion by abstraction of a proton from the aldehyde. The Mannich reaction with ketones, which is accelerated by decrease of pH, proceeds by an electrophilic substitution mechanism (S_E2) with intermediate formation of a carbonium-imonium ion $[R_2N-\overset{+}{C}H_2 \leftrightarrow \leftrightarrow R_2\overset{+}{N}=CH_2]$, which is in fact the aminomethylating agent in this case.

The hydrochlorides of the Mannich bases obtained with ketones are more stable to heat than those obtained with aldehydes; the latter are decomposed to form unsaturated aldehydes on heating the aqueous solution to 90-100°, while the former require temperatures of the order of 150-200°. To decrease losses of the vinyl ketones by polymerisation the decomposition has been carried out under vacuum. Technological processes have been developed in principle for the production of methyl vinyl ketone and isopropenyl methyl ketone.

Recent work has thus shown that α,β-unsaturated ketones can be obtained by the Mannich reaction between formaldehyde and ketones in yields close to theoretical. Advantages of this process are the practically complete conversion of the starting materials per pass, the simplicity of the apparatus, the high yields of the vinyl ketones, and the absence of side reactions, which considerably simplifies the isolation of the vinyl ketones formed. Because of all this the process can be readily worked industrially.

This method has been employed for the production of methyl vinyl ketone [214,217,222], isopropenyl methyl ketone [214,215,222], 2-thienyl vinyl ketone [158], isopropenyl 2-thienyl ketone [158], phenyl vinyl ketone [158,212,217,221], isopropenyl phenyl ketone [213,218,222], 1-ethylvinyl phenyl ketone [213], isopropenyl ethyl ketone [215], 1-isopropylvinyl methyl ketone [215], *m*- and *p*-nitrophenyl vinyl ketones [219,220], and others.

In subsequent work Farberov and coworkers [172,226] have used the Mannich reaction to develop a new method for the production of divinyl ketones, which are of considerable interest as cross-linking agents for high-molecular compounds and as starting materials for other syntheses.

The Mannich reaction is applicable to the production of a large number of carbonyl monomers [168-173,224-226], and this is another advantageous feature of the process.

1. Chem. Eng., 56 (11), 67 (1949).
2. Chem. Eng., 57 (4), 183 (1950).
3. U.S.P. 2 991 305 (1961).
4. S.A.Ballard, H.de V.Finch, and D.E.Winkler, Adv.Catalysis, 9, 754 (1957).
5. T.P.Forbeth and B.J.Jaffney, Petrol.Refiner, 34, 160 (1955).
6. B.P. 619 014 (1949).
7. M.Mugdan and D.P.Joung, J.Chem.Soc., 2988 (1949).
8. M.Jreville, Ind.Chemist, 37, 15 (1961).
9. Oil and Gas J., 57 (26), 80 (1959).
10. Chem.Age, 83, 648 (1960).
11. M.A.Dalin, "Neftekhimicheskie Sintezy" (Petroleum-Chemical Syntheses), Goskhimizdat, 1961, p.76.
12. S.A.Ballard, H.D.Finch, B.P.Geyer, G.W.Hearne, C.W.Smith, and R.R.Whetstone, in "Fourth World Petroleum Congress, Rome, 1955, Proceedings, Sect.IV" pp.141-154; Russian translation, Vol.5, Gostoptekhizdat, 1956, p.181.
13. German P. 869 950 (1953).
14. B.P. 740 005 (1955).
15. C.W.Smith and R.T.Holm, J.Org.Chem., 22, 746 (1957).
16. H.Keyiti, Chem.Eng.(Japan), 3, 981 (1958).
17. H.Keyiti, Chem.Eng.(Japan), 4, 40 (1959).
18. H.Keyiti, Chem.Eng.(Japan), 5, 138 (1959).
19. J.Kuchenbuch, Kunststoff-Rundschau, 6, No.11, 490 (1959).
20. C.W.Smith (Editor), "Acrolein", Wiley, New York, 1962.
21. W.Kern and R.Schulz, Angew.Chem., 69, 163 (1957).
22. P.W.Sherwood, World Petroleum, 31, No.12, 60 (1960).
23. R.E.Kirk and D.E.Othmar (Editors), "Encyclopaedia of Chemical Technology", First Supplement Volume, Interscience, New York, 1957, p.6.
24. H.J.Sanders, G.O.Walker, H.S.Edwards, and T.J.Hall, Ind.Eng.Chem., 50, 854 (1958).
25. H.J.Sanders, G.O.Walker, H.S.Edwards, and T.J.Hall, Chemie et Industrie, 82, 848 (1959).
26. J.M.Church and L.Lynn, Ind.Eng.Chem., 42, 768 (1950).
27. U.S.P. 2 767 221 (1956).
28. U.S.P. 2 744 928 (1956).
29. U.S.P. 2 779 801 (1957).

30. W.F.Brill and F.Lister, J.Org.Chem., 26, 565 (1961).
31. P.Wazulik, "Chemistry of Monomers" (Translated into Russian), Inostr.Lit., Moscow, 1, 359 (1960).
32. G.T.Morgan, N.J.L.Megson, and K.W.Pepper, Chem.and Ind., 57, 885 (1938).
33. German P. 745 032 (1943).
34. U.S.P. 2 005 295 (1935).
35. U.S.P. 2 404 817 (1946).
36. B.P. 585 396 (1947).
37. B.N.Rutovskii and N.Yakobson, Zhur.Prikl.Khim., 14, 528 (1941).
38. B.N.Rutovskii and A.Dmitrieva, Zhur.Prikl.Khim., 14, 535 (1941).
39. B.N.Rutovskii and G.S.Goncharov, Zhur.Prikl.Khim., 14, 542 (1941).
40. E.C.Chapin, J.E.Ham, and C.L.Mills, J.Polymer Sci., 4, 597 (1949).
41. U.S.P. 2 332 897 (1944).
42. C.W.Gould and G.E.Hulse, Ind.Eng.Chem., 41, 1021 (1949).
43. C.W.Gould, L.O.Amberg, and G.E.Hulse, Ind.Eng.Chem., 41, 1025 (1949).
44. U.S.P. 2 386 447 (1945).
45. French P. 802 499, 802 500 (1936).
46. U.S.P. 2 278 415 (1942).
47. C.S.Marvel, J.Polymer Sci., 8, 495 (1952).
48. "Synthetic Rubber" (Edited by G.S.Whitby, C.C.Davis, and R.F.Dunbrook) (Translated into Russian), GKhI, Leningrad, 1957, p.714.
49. H.Schulz and H.Wagner, Angew.Chem., 62, 105 (1950).
50. F.G.Watson, Chem.Eng., 54, 106 (1947).
51. C.R.Nelson and M.L.Courter, Chem.Eng.Progr., 50, 526 (1954).
52. German P. 825 836 (1949).
53. F.Asinger, "Einführung in die Petrolchemie" (Translated into Russian), Gostoptekhizdat, 1961, p.171.
54. Chem.Age, 62, No.1591, 13 (1950).
55. Ital.P. 596 748 (1959).
56. B.P. 847 564 (1960).
57. Chem.Eng.News, 39, No.41, 56 (1961).
58. Chem.Age, 86, No.2206, 634 (1961).
59. USSR P. 131 347 (1960); Chem.Abs., 55, 6377 (1961).
60. USSR P. 143 385 (1962); Ref.Zhur.Khim., 19L45 (1962).
61. N.I.Popova, V.I.Belyaeva, and R.N.Stukova, Izv.Vost.-Sib. Fil.Akad.Nauk SSSR, No.7, 40 (1957).
62. O.V.Isaev, M.Ya.Kushnerov, and L.Ya.Margolis, Dokl. Akad.Nauk SSSR, 119, 1104 (1958).
63. O.V.Isaev and M.Ya.Kushnerov, Dokl.Akad.Nauk SSSR, 124, 858 (1959).
64. O.V.Isaev, L.Ya.Margolis, and S.Z.Roginskii, Zhur. Obshch.Khim., 29, 1522 (1959).
65. O.V.Isaev, L.Ya.Margolis, and I.S.Sazonova, Dokl.Akad. Nauk SSSR, 129, 141 (1959).
66. V.M.Belousov, Ya.B.Gorokhovatskii, M.Ya.Rubanik, and A.V.Gershingorina, Dokl.Akad.Nauk SSSR, 132, 1125 (1960).
67. Yu.D.Kernos and B.L.Moldavskii, Zhur.Prikl.Khim., 33, 2593 (1960).
68. B.L.Moldavskii, V.P.Teodorovich, and Yu.D.Kernos, in "Sbornik: Trudy Soveshchaniya po Khimicheskoi Pererabotke Neftyanykh Uglevodorodov v gorode Baku v 1957 g" (Proceedings of the Congress on the Chemical Treatment of Petroleum Hydrocarbons, Baku, 1957), Izd.Akad.Nauk Azerb.SSR, 1960, p.171.
69. O.V.Isaev and L.Ya.Margoliz, Kinetika i Kataliz, 1, 237 (1960).
70. N.I.Popova and E.E.Vermel', Dokl.Akad.Nauk SSSR, 124, 842 (1959).
71. V.M.Belousov, Ya.B.Gorokhovatskii, M.Ya.Rubanik, and A.V.Gershingorina, Dokl.Akad.Nauk SSSR, 137, 1396 (1961).
72. B.V.Kir'yan, S.S.Babkov, Yu.A.Kozlova, and I.M.Borzova, in "Doklady na Vsesoyuznoi Konferentsii po Organicheskomy Katalizu, Tezisy" (Reports to the All-Union Conference on Organic Catalysis, Abstracts), Izd.Akad.Nauk SSSR, Moscow, 1959, p.64.
73. E.Kh.Enikeev, O.V.Isaev, and L.Ya.Margolis, Kinetika i Kataliz, 1, 431 (1960).
74. Ya.B.Gorokhovatskii, M.Ya.Rubanik, and E.N.Popova, Kinetika i Kataliz, 3, 133 (1962).
75. V.M.Belousov, Ya.B.Gorokhovatskii, and M.Ya.Rubanik, Kinetika i Kataliz, 3, 221 (1962).
76. N.I.Popova and E.E.Vermel', Izv.Sib.Otd., Akad.Nauk SSSR, (11), 89 (1960).
77. N.I.Popova, R.N.Stepanova, and R.N.Stukova, Kinetika i Kataliz, 2, 916 (1961).
78. V.I.Belyaev and R.N.Stukova, Ref.Rabot Labor.Organich. Sinteza Vost.Sib.Fil.Akad.Nauk SSSR, 1956.
79. L.Ya.Margolis, S.Z.Roginskii, and G.A.Gracheva, Zhur. Obshch.Khim., 26, 1368 (1956).
80. O.V.Isaev, M.Ya.Kushnerov, and L.Ya.Margolis, Dokl. Akad.Nauk SSSR, 119, 102 (1958).
81. V.P.Latyshev and N.I.Popova, Izv.Sib.Otd., Akad.Nauk SSSR, (9), 48 (1959).
82. Ya.B.Gorokhovatskii, E.N.Popova, and M.Ya.Rubanik, Kinetika i Kataliz, 3, 230 (1962).
83. M.M.Kaliberdo, V.A.Pilosyan, and N.I.Popova, Kinetika i Kataliz, 3, 237 (1962).
84. N.I.Popova, E.E.Vermel', and F.A.Mil'man, Kinetika i Kataliz, 3, 241 (1962).
85. B.D.Kruzhalov, E.S.Shestukhin, and A.M.Garnish, Kinetika i Kataliz, 3, 247 (1962).
86. A.G.Polkovnikova, B.D.Kruzhalov, L.N.Shatalova, and L.L.Tseitina, Kinetika i Kataliz, 3, 252 (1962).
87. A.M.Garnish, L.M.Shafranskii, N.P.Skvortsov, E.A.Zvezdina, and V.F.Stepanovskaya, Kinetika i Kataliz, 3, 257 (1962).
88. N.I.Popova, F.A.Mil'man, R.N.Stukova, and K.P.Zhdanova, Izv.Sib.Otd., Akad.Nauk SSSR, (12), 78 (1960).
89. N.I.Popova, R.N.Stukova, and V.P.Latyshev, Izv.Sib.Otd., Akad.Nauk SSSR, (8), 78 (1961).
90. L.N.Kutseva and L.Ya.Margolis, Zhur.Obshch.Khim., 32, 102 (1962).
91. O.A.Golovina, O.V.Isaev, and M.M.Sakharov, Dokl.Akad. Nauk SSSR, 142, 619 (1962).
92. P.W.Sherwood, Chimie et Industrie, 85, 401 (1961).
93. P.W.Sherwood, Chimie et Industrie, 87, 764 (1962).
94. P.W.Sherwood, Ind.Chemist, 38, No.444, 55 (1962).
95. U.S.P. 2 627 527 (1953).
96. U.S.P. 2 451 485 (1948).
97. Jap.P. 6357 (1957); Chem.Abs., 52, 12 896 (1958).
98. U.S.P. 2 670 379 (1954).
99. B.P. 694 362 (1953).
100. U.S.P. 2 753 377 (1956).
101. Jap.P. 7459 (1960); Ref.Zhur.Khim., 24L64 (1961).
102. U.S.P. 2 776 316 (1957).
103. U.S.P. 2 662 921 (1953).
104. B.P. 873 712 (1959).
105. Australian P. 149 819 (1953).
106. U.S.P. 2 383 711 (1945).
107. U.S.P. 2 643 269 (1953).
108. U.S.P. 2 669 586 (1954).
109. U.S.P. 2 670 380 (1954).
110. U.S.P. 2 941 007 (1960).
111. B.P. 828 812 (1960).
112. U.S.P. 2 670 381 (1954).
113. German P. 880 133 (1953).
114. B.P. 821 999 (1959).
115. U.S.P. 2 847 475 (1958).

116. U.S.P. 2659758 (1953).
117. U.S.P. 2608585 (1952).
118. U.S.P. 2627527 (1953).
119. U.S.P. 2879300 (1959).
120. B.P. 778125 (1957).
121. B.P. 777010 (1957).
122. U.S.P. 2670381 (1954).
123. U.S.P. 2716664 (1955).
124. B.P. 805776 (1958).
125. N.I.Popova, F.A.Mil'man, and L.E.Latysheva, Izv.Sib. Otd., Akad.Nauk SSSR, (7), 77 (1961).
126. USSR P. 136728 (1961); Ref.Zhur.Khim., 3L87 (1962).
127. Canad.P. 511044 (1955).
128. B.P. 878803 (1959).
129. M.Kitahara and F.Moriya, Reports Inst.Phys.Chem.Res. (Japan), 38, 45 (1962).
130. M.Kitahara and F.Moriya, Reports Inst.Phys.Chem.Res. (Japan), 38, 51 (1962).
131. M.Kitahara and T.Konishi, Reports Inst.Phys.Chem.Res. (Japan), 38, 57 (1962).
132. M.Kitahara and T.Konishi, Reports Inst.Phys.Chem.Res. (Japan), 38, 64 (1962).
133. Jap.P. 10962 (1961); Chem.Abs., 56, 4621 (1962).
134. "Ullmanns Ensyklopedia der technischen Chemie", 3.Aufl., 3, 72 (1952).
135. P.W.Sherwood, Petrol Refiner, 35, No.12, 157 (1956).
136. French P. 847370 (1939).
137. U.S.P. 2294955 (1942).
138. N.S.Dabagov, I.S.Travkin, L.K.Kazakevich, and F.A.Tokareva, Trudy Nauch.-Issled.Inst.Sint.Spirta, 1, 121 (1959).
139. S.Malinowski, H.Jedrzejewska, S.Basinski, Z.Lipski, and J.Moszczenska, Roczniki Chem., 30, 1129 (1956).
140. S.Malinowski, H.Jedrzejewska, S.Basinski, and Z.Lipski, Roczniki Chem., 31, 71 (1957).
141. S.Malinowski, S.Basinski, M.Olszewska, and H.Zieleniewska, Roczniki Chem., 31, 123 (1957).
142. S.Malinowski, H.Jedrzejewska, S.Basinski, and Z.Lipski, Roczniki Chem., 32, 203 (1958).
143. S.Basinski and S.Malinowski, Przemysl Chem., 38, 164 (1959).
144. S.Malinowski, H.Jedrzejewska, S.Basinski, and S.Benbenek, Rev.Chim.(Acad.R.P.R), 6, 5 (1961).
145. S.Malinowski and S.Basinski, Przemysl Chem., 41, 202 (1962).
146. Jap.P. 3728 (1951); Chem.Abs., 47, 8089 (1953).
147. T.Ishikawa, Tokyo Kôgyô Shikensho Hôkoku, 52, 347 (1957).
148. T.Ishikawa and Ts.Kamio, J.Soc.Organ.Synth.Chem. Japan, 20, 56 (1962).
149. S.Malinowski, H.Jedrzejewska, S.Basinski, and S.Benbenek, Chemie et Industrie, 85, 885 (1961).
150. U.S.P. 2288306 (1942).
151. German P. 888541 (1953).
152. U.S.P. 2549457 (1951).
153. German P. 857951 (1952).
154. B.Reicher, "Die Mannich-Reaktion", Springer, Berlin, 1959.
155. H.Hellmann and G.Opitz, "α-Aminoalkylierung", Verlag Chemie, Weinheim, 1960.
156. C.Mannich, B.Lesser, and F.Silten, Ber., 65, 378 (1932).
157. C.Mannich and S.Abdullach, Ber., 68, 113 (1935).
158. F.F.Blick and J.H.Burckhalter, J.Amer.Chem.Soc., 64, 451 (1942).
159. A.N.Kost and V.V.Ershov, Zhur.Obshch.Khim., 27, 1072 (1957).
160. German P. 875194 (1939).
161. German P. 867852 (1943).
162. U.S.P. 2518416 (1950).
163. U.S.P. 2639295 (1953).
164. U.S.P. 2848499 (1958).
165. C.S.Marvel, R.L.Myers, and J.H.Saunders, J.Amer. Chem.Soc., 70, 1694 (1948).
166. M.B.Green and W.J.Hickinbottom, J.Chem.Soc., 3262 (1957).
167. M.M.Koton, I.V.Andreeva, and Yu.P.Getmanchuk, Vysokomol.Soed., 4, 1537 (1962).
168. M.I.Farberov, G.S.Mironov, M.A.Korshunov, E.P.Tepenitsyna, E.N.Shkarnikova, and V.D.Zav'yalov, USSR P. 144164 (1962); Byull.Izobretenii, (2), 17 (1962).
169. M.I.Farberov, G.S.Mironov, and M.A.Korshunov, Zhur. Prikl.Khim., 35, 2483 (1962).
170. G.S.Mironov, M.I.Farberov, and M.A.Korshunov, Khim.i Khim.Tekhnol., Yaroslavl', 1 (8), 33 (1962).
171. M.I.Farberov and G.S.Mironov, Kinetika i Kataliz, 4, 526 (1963).
172. M.I.Farberov and G.S.Mironov, Dokl.Akad.Nauk SSSR, 148, 1095 (1963).
173. G.S.Mironov, Candidate's Thesis, Yaroslavl' Technological Inst., Yaroslavl', 1962.
174. G.S.Mironov, M.I.Farberov, and I.I.Bespalova, Zhur. Obshch.Khim., 34, 1642 (1964).
175. A.A.Berlin, Uspekhi Khim., 8, 1849 (1939).
176. J.A.Nieuwland and W.L.Foohey, Proc.Indiana Acad.Sci., 38, 196 (1929).
177. J.A.Nieuwland, W.S.Calcott, F.B.Downing, and A.S.Cartor, J.Amer.Chem.Soc., 53, 4197 (1931).
178. A.P.Churbakov and V.N.Ryazantsev, Zhur.Prikl.Khim., 13, 1464 (1940).
179. A.P.Churbakov and V.N.Ryazantsev, Prom.Org.Khim., 7, 663 (1940).
180. German P. 926007 (1955).
181. B.P. 508080 (1939).
182. U.S.P. 2265177 (1942).
183. U.S.P. 2371577 (1945).
184. U.S.P. 2400409 (1946).
185. A.Gorin and L.P.Bogdanova, Zhur.Obshch.Khim., 28, 657 (1958).
186. A.Gorin and L.P.Bogdanova, Zhur.Obshch.Khim., 28, 1144 (1958).
187. K.A.Ogloblin, Zhur.Obshch.Khim., 18, 2153 (1948).
188. U.S.P. 2524865 (1950).
189. U.S.P. 2524866 (1950).
190. E.M.McManon, J.N.Roper, W.P.Utermohler, R.H.Hasek, R.C.Harris, and J.H.Brant, J.Amer.Chem.Soc., 70, 2971 (1948).
191. U.S.P. 2245567 (1941).
192. S.Malinowski, S.Benbenek, J.Pasynkiewicz, and E.Wojciechowska, Roczniki Chem., 32, 1089 (1958).
193. U.S.P. 2549508 (1951).
194. USSR P. 137510 (1961); Ref.Zhur.Khim., 2L69 (1962).
195. G.T.Morgan and E.L.Holmes, J.Chem.Soc., 2667 (1932).
196. T.W.White and R.N.Haward, J.Chem.Soc., 25 (1943).
197. N.A.Milas, E.Sakal, J.T.Plati, J.T.Rivers, J.K.Gladding, F.X.Grossi, Z.Weiss, M.A.Campbell, and H.F.Wright, J.Amer.Chem.Soc., 70, 1597 (1948).
198. V.Kabaivanov, M.Mikhailov, and L.B.Bozveliev, Godishnik, Khim.Tekhnol.Inst., 1, 13 (1954).
199. U.S.P. 2387933 (1945).
200. N.Murata, H.Arai, and M.Tanaka, J.Chem.Soc.Japan, Ind.Chem.Sect., 60, 1206 (1957).
201. E.D.Bergmann, R.Ikan, and H.Weiler-Feilchenfeld, Bull. Soc.chim.France, 290 (1957).
202. J.Bolle, H.Jean, and T.Jullig, Mém.Services chim.État, 34, 321 (1948).
203. T.J.Hays, G.T.Hager, H.M.Engelmann, and H.M.Spurlin, J.Amer.Chem.Soc., 71, 5369 (1951).
204. H.Staudinger and Ritzenhalter, 67, 1773 (1934).

205. U.S.P. 2380828 (1945).
206. E.F.Landau and E.P.Irany, J.Org.Chem., 12, 422 (1947).
207. B.P. 783458 (1957).
208. B.P. 833666 (1960).
209. P.Reynaud and J.Matti, Compt.rend., 236, 2156 (1953).
210. C.Mannich and P.Hönig, Arch.Pharm., 265, 598 (1927).
211. C.Mannich and J.Heilner, Ber., 55, 356 (1922).
212. W.G.Young and J.D.Roberts, J.Amer.Chem.Soc., 68, 649 (1946).
213. J.H.Burckhalter and R.C.Fuson, J.Amer.Chem.Soc., 70, 4184 (1948).
214. H.J.Hagemeyer, J.Amer.Chem.Soc., 71, 1119 (1949).
215. R.Heilmann, G.de Gaudemaris, and P.Arnaud, Compt. rend., 234, 1177 (1962).
216. A.M.Shur, Neftekhimiya, 2, 600 (1962).
217. A.V.Logan, J.L.Huston, and D.L.Dorward, J.Amer.Chem. Soc., 73, 2952 (1951).
218. H.Riviere-Larramona, Compt.rend., 244, 1654 (1957).
219. Kao Yee-sheng, Hsu Hsiu-yong, Chen Chi-hao, Loh Shuen--hsing, Owen Tsung-yao, Pan Pei-chuan, and Chen Jen--lien, Sci.Sinica, 6, 1031 (1957).
220. Kao Yee-sheng, Hsu Hsiu-yong, Chen Chi-hao, Loh Shuen--hsing, Owen Tsung-yao, Pan Pei-chuan, and Chen Jen-lien, Acta Chim.Sinica, 23, 385 (1957).
221. A.Ya.Yakubovich, V.V.Razumovskii, and I.N.Belyaeva, Zhur.Obshch.Khim., 28, 680 (1958).
222. German P. 877606 (1953).
223. P.Wazulik, "Chemistry of Monomers" (Translated into Russian), Vol.1, Inostr.Lit., Moscow, 1960, p.350.
224. G.S.Mironov, M.I.Farberov, and I.M.Orlova, Zhur.Prikl. Khim., 36, 654 (1963).
225. M.I.Farberov and G.S.Mironov, USSR P. 154256 (1963); Byull.Izobretenii i Tov.Znakov, (9), 21 (1963).
226. G.S.Mironov, M.I.Farberov, and I.M.Orlova, Zhur. Obshch.Khim., 33, 1512 (1963).

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CATALYTIC REDUCTION OF DINITRILES

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I. INTRODUCTION

As a result of the extensive industrial applications of the polymeric condensation of bifunctional compounds, a great deal of research has been done in recent years on methods of preparation of diamines. Of these, the catalytic reduction of dinitriles to diamines seems to hold the greatest promise.

Several papers have also been published on the partial reduction of dinitriles. The preparation of ω-amino-acid nitriles by catalytic hydrogenation of dinitriles may become important as a simple route to ω-amino-acids and lactams, particularly caprolactam.

In spite of the many patents and papers on the catalytic reduction of dinitriles, the field has not been reviewed up to the present.

II. REACTION CONDITIONS

The hydrogenation conditions of aliphatic, aromatic, and organosilicon dinitriles are summarised in Table 1. The reduction catalyst used is invariably a Group VIII metal: palladium activated by platinum oxide[1], Raney nickel and cobalt[2-33], nickel and cobalt catalysts on a carrier[34-39], and also nickel boride[40,41] and cobalt boride[41,42] catalysts, prepared by reduction to the metal of a salt in aqueous solution, using sodium tetrahydroborate[42].

In the presence of noble metals, the reaction proceeds rapidly at room temperature and under hydrogen pressures close to 1 atm.[1] Nickel and cobalt catalysts require elevated temperatures and hydrogen pressures. The dinitrile of adipic acid can be hydrogenated under milder conditions on a Raney nickel than on a Raney cobalt catalyst[7,8]. Cobalt catalysts are the more stable, and the more selective towards formation of a primary diamine. Raney nickel retained its activity for 30–35 h without regeneration[7] in the reduction of the adipodinitrile under flow conditions, whereas Raney cobalt and Co/Al_2O_3 retained it for ~ 500 h.[8,39]

Raney nickel–copper catalysts were found to be appreciably less active towards hydrogenation of the adipodinitrile[46]. Raney iron also has a low catalytic activity: the dinitrile of terephthalic acid is reduced to a negligible extent in the presence of this catalyst[13]. Thus the activity of metallic catalysts towards the reduction of dinitriles decreases in the sequence: Pt, Pd > Ni > Co > Fe, Cu. The reaction is usually carried out in the liquid phase, in a medium of ammonia[2-8,18-43] or of an inert solvent (alcohol, dioxan) saturated with ammonia[9-17].

By studying the catalytic reduction of the dinitriles of adipic, sebacic, terephthalic, isophthalic, and *p*- and *m*-phenylenediacetic acids it has been shown that an ammoniacal medium favours the formation of primary amines and lowers the yield of secondary and tertiary amines[10-12,17].

However, the reduction of the second nitrile group of adipodinitrile is hindered[3] at very high concentrations of ammonia, and a significant amount of the partial hydrogenation product (6-aminocapronitrile) is formed in addition to hexamethylenediamine.

In a solution of sodium acetate in acetic anhydride at 50° and under a hydrogen pressure of 3.5 atm, hexamethylenediamine was formed on Raney nickel in almost quantitative yield, but the catalyst rapidly lost its activity and disintegrated. Under the same conditions, the yield of