Chemistry of the Production of Organic Isocyanates

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1 Introduction

The manufacture of organic isocyanates has grown at a rapid rate in the past twenty years and world productive capacity now stands at over 1 000 000 tons per annum. The reactivity of isocyanates and the versatility of derived polymers ensures increasing demand for them and new plants continue to be erected. The complexity of the plants and the hazards associated with the raw materials and the products themselves have restricted production to the larger chemical companies whose resources are adequate to deal with many of the chemical and engineering problems arising in manufacture. Much of the information relating to isocyanate production is described only in patent specifications. The large number of patents issued and the breadth of the claims contained in them makes it difficult for scientists not directly involved in manufacture to get a clear idea how processes are operated.
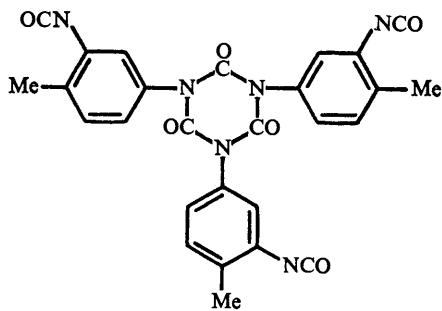
At least 90% of total world production is accounted for by two products, tolylene di-isocyanate (TDI) and diphenylmethane di-isocyanate (MDI). Small amounts of other di-isocyanates are made, including 1,6-hexamethylene di-isocyanate, 1,5-naphthalene di-isocyanate, xylylene di-isocyanate, 4,4'-dicyclohexylmethane di-isocyanate and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate. Also manufactured are various monoisocyanates, including methyl, n-propyl, n-butyl, cyclohexyl, phenyl, and 4-chloro- and 3,4-dichloro-phenyl isocyanates. The di-isocyanates are used to make urethane polymers such as foams, elastomers, surface coatings and fibres. The monoisocyanates are used for substituted ureas and carbamates important as herbicides and crop protection agents.

Some of the basic di-isocyanates are converted on a commercial scale into derived products containing residual isocyanate groups. Thus TDI is trimerized and sold as a solvent solution of its trifunctional isocyanurate (1), and hexamethylene di-isocyanate is converted into the substituted biuret (2). Di-isocyanates may also be treated with deficiencies of diols (HOXOH) to give non-volatile bis-carbamates (3) containing terminal isocyanate groups.

The manufacture of these latter products is not discussed in this article, which is restricted to describing the chemistry of the processes used for the main commercial di-isocyanates.
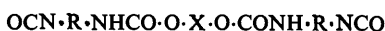
2 Preparation of Isocyanates

Isocyanates can be made in many ways; the classical laboratory routes, the

(1)

$$OCN(CH_2)_6NCONH(CH_2)_6NCO$$
$$|$$
$$CONH(CH_2)_6NCO$$

(2)

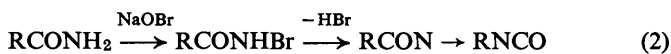$$OCN \cdot R \cdot NHCO \cdot O \cdot X \cdot O \cdot CONH \cdot R \cdot NCO$$

(3)

Curtius, Hoffman, and Lossen rearrangements (reactions 1, 2, 3), which may involve a nitrene as an intermediate, are not at all satisfactory for large-scale operation.

$$RCOCl \xrightarrow{NaN_3} RCON_3 \xrightarrow{-N_2} RCON \rightarrow RNCO \qquad (1)$$

$$RCONH_2 \xrightarrow{NaOBr} RCONHBr \xrightarrow{-HBr} RCON \rightarrow RNCO \qquad (2)$$

$$R^1COOR^2 \xrightarrow{NH_2OH} R^2OH + R^1CONHOH \xrightarrow{-H_2O} R^1CON \rightarrow R^1NCO \qquad (3)$$

The use of azides in the Curtius reaction is hazardous and the utility of the Hoffmann and Lossen rearrangements is limited to preparation of aliphatic isocyanates as, in the aqueous media employed, aromatic isocyanates react readily with water to form substituted ureas. t-Butyl hypochlorite can be used for non-aqueous Hoffmann rearrangements but is too costly for technical applications.

In practice, only phosgenation of a primary amine is important (reaction 4). This route, first used by Hentschel[1] in 1884, enables a wide range of aliphatic and aromatic isocyanates to be obtained from the corresponding amines. The laboratory preparation of numerous examples by this method has been described by Siefken.[2]

$$RNH_2 \xrightarrow{COCl_2} RNHCOCl \xrightarrow{-HCl} RNCO \qquad (4)$$
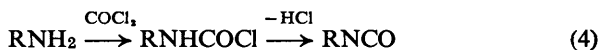
[1] W. Hentschel, *Ber.*, 1884, **17**, 1284.
[2] W. Siefken, *Annalen*, 1949, **562**, 75.

3 The Phosgenation of Primary Amines

Relatively little detailed attention has been given to phosgenation processes other than those for tolylene di-isocyanate and diphenylmethane di-isocyanate, but it is generally considered that the mechanism of the phosgenation reaction and the pattern of impurities resulting from side reactions is similar for many amines, both aromatic and aliphatic in nature.

Phosgenation of a primary amine is usually carried out by dissolving it in an inert solvent before treating with phosgene. As an alternative the amine may first be converted into a suspension of a salt by passing dry hydrogen chloride or carbon dioxide into the solution before contacting with phosgene. Improved results are sometimes claimed for this procedure although, as a rule, phosgenation of pre-formed salts is slower than direct reaction of the amine. Relatively volatile monoamines, *e.g.* cyclohexylamine or aniline, can be phosgenated quite satisfactorily using a vapour-phase method; an inert gas carrier is sometimes used. Typical processes have been patented by ICI and Bayer.[3]

Another variation is sometimes referred to as 'interfacial' phosgenation. An aqueous solution of a primary amine and an acid acceptor, such as an inorganic alkali or a tertiary amine, is added to an agitated solution of phosgene in a water-immiscible organic solvent. The aqueous phase is discarded and the isocyanate recovered from the organic solvent. The method is unsuitable for aromatic isocyanates because of the readiness with which they react with water, but it is useful for aliphatic isocyanates which are hydrolysed only slowly. The procedure is particularly useful for phosgenating primary amines containing unsaturated bonds sensitive to the action of hydrogen chloride present in solvent or vapour-phase phosgenation.[4]

The solvent used as reaction medium must be inert to phosgene, hydrogen chloride, and the isocyanate being prepared. Chloro- and dichloro-benzene are frequently used as they are sufficiently high boiling to allow suitably high reaction temperatures to be attained. Overall reaction rates and yields can be increased by using more polar solvents such as ketones and esters, although neither type is satisfactory for large-scale use; hydrogen chloride is highly soluble in them and mild or stainless steel plant is rapidly corroded when they are used.

Isocyanates take part in very many reactions[5] and in consequence they are difficult to prepare in high yield and purity. The methods used and the chemistry involved in the successful large-scale production of isocyanates are described below.

Tolylene Di-isocyanate.—The isocyanate at present manufactured in largest quantity is tolylene di-isocyanate. The commercial material, a colourless liquid boiling at 251 °C, is a mixture of the 2,4- and 2,6-isomers, the product containing 80% of the former being in greatest demand. Toluene is treated with a mixture

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[3] Bayer, U.S.P. 2 823 221; ICI, B.P. 1 165 831.

[4] ICI, B.P. 1 152 877; B.P. 1 208 862.

[5] J. H. Saunders and R. J. Slocombe, *Chem. Rev.*, 1948, **43**, 204; R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *ibid.*, 1957, **57**, 47; S. Ozaki, *ibid.*, 1972, **72**, 457.

of nitric and sulphuric acids to give dinitrotoluene, usually in a continuous operation; the product is separated from the 'spent' acid, neutralized and washed thoroughly. Small amounts of nitrocresols can be produced during nitration and conditions are selected to minimize their formation as they can act as catalyst poisons in the subsequent hydrogenation stage. The product comprises approximately 76% 2,4-, 19% 2,6-, 2.5% 3,4-, 1.5% 2,3- and 1.0% 3,6-dinitrotoluene.

The mixture of isomeric dinitrotoluenes was originally reduced to tolylene diamine with iron and aqueous acid but catalytic hydrogenation is now used. This is usually performed under pressure in an alcohol solvent with either a nickel or a palladium catalyst.[6] A high yield is obtained and after filtration the solution is concentrated; the diamine may be distilled to remove some tar. Deamination to 4-toluidine occurs to a small extent. The boiling point of the mixed diamines is *ca.* 178 °C at 30 mmHg.

As explained later, the presence of 2,3- and 3,4-diamines is disadvantageous as they are responsible for loss of yield and quality defects in the finished products. The iron reduction process eliminated *ortho*-diamines by forming involatile iron co-ordination complexes. Catalytic hydrogenation, however, gives higher yields of the *meta*-diamines and is easier to operate. Manufacturers therefore minimize formation of *ortho*-compounds or remove them at some stage. The process used by a particular company is usually not disclosed but many methods for reducing the content of *ortho*-diamines have been patented. Purification by crystallization is too costly for large-scale operation but separation of isomers by fractional distillation has been claimed as satisfactory in a patent.[7] It is also possible to eliminate *ortho*-isomers by adding compounds which react preferentially with *ortho*-amino-groups to give derivatives which are stable but involatile under the distillation conditions for the *meta*-diamines. Typical additives include boric acid,[8] oxalic acid and its esters,[9] urea,[10] carbon disulphide,[11] and tolylene di-isocyanate residues;[12] *e.g.* the reaction with urea results in the formation of a high melting methylbenzimidazolone (4).

(4)
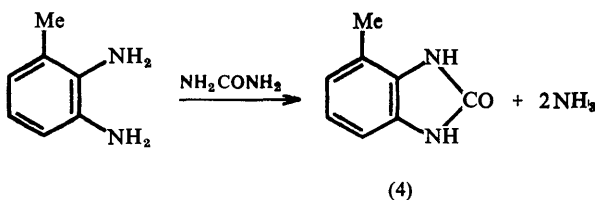
Scheme 1

[6] Bayer, B.P. 821 220; ICI, B.P. 907 154.
[7] Allied Chemical Corpn., B.P. 1 133 668.
[8] ICI, B.P. 966 812.
[9] ICI, B.P. 982 483.
[10] Mobay, B.P. 1 145 431.
[11] F.M.C. Corpn., U.S.P. 3 134 813.
[12] F.M.C. Corpn., U.S.P. 3 246 035.

Phosgenation of Tolylene Diamine. Tolylene diamine was originally phosgenated 'batchwise' by adding a solution of it, *e.g.* in a halogenated aromatic solvent, to a stirred reactor containing a solution of phosgene in the same solvent. After completion of addition the reactor was heated to 150—200 °C with gaseous phosgene passing until no more hydrogen chloride was evolved. Better yields are now obtained using continuous processes with a series of stirred vessels. Phosgenation in this way was first described by Bayer[13] and modifications of the basic process are still in use today.
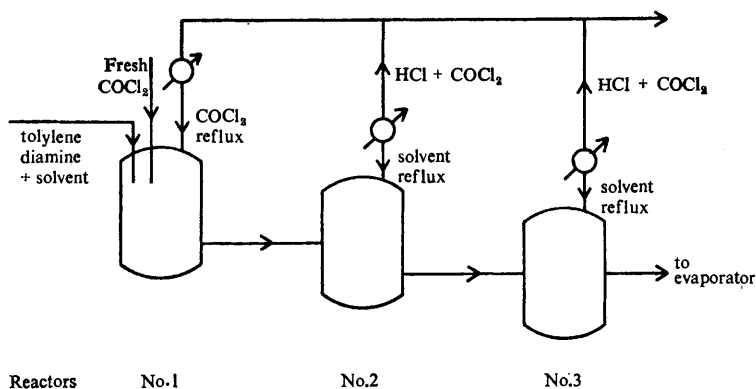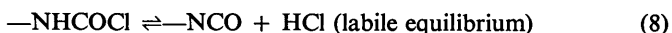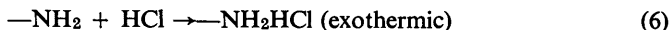

Figure 1 *Continuous phosgenation of a primary amine*

In the continuous process (Figure 1) the tolylene diamine mixed isomers are dissolved in an inert solvent such as chloro- or dichloro-benzene, and added continuously together with excess liquid phosgene to a well-agitated first-stage reactor. Conditions of temperature and pressure and reactor design vary from one manufacturer to another. The reactor may be fitted with cooling jackets or internal coils to control the highly exothermic initial reaction (-37.5 kcal mol^{-1} diamine). Alternatively, a very large excess of phosgene (b.p. 8 °C) may be used and allowed to reflux to achieve the same purpose. No satisfactory study of the kinetics of the very rapid reaction of tolylene diamine with phosgene has been published. Model systems using monoamines have been examined but these are considered to have little relevance to the technical systems involving phosgenation of polyamines.

The reaction mixture flows continuously from the first reactor to a second, third, or even fourth-stage reactor. Residual phosgene and hydrogen chloride are removed from the solution of crude isocyanate which is then concentrated and finally distilled to give a technically pure product.

Reactions taking place in the first-stage reactor. The reactions taking place in the first-stage reactor may be summarized as follows:

[13] Bayer, Ger. P. 844 896.

213

$$—NH_2 + COCl_2 \rightarrow —NHCOCl + HCl \text{ (exothermic)} \qquad (5)$$

$$—NH_2 + HCl \rightarrow —NH_2HCl \text{ (exothermic)} \qquad (6)$$

$$—NH_2 + —NHCOCl \rightarrow —NCO + —NH_2,HCl \qquad (7)$$

$$—NHCOCl \rightleftharpoons —NCO + HCl \text{ (labile equilibrium)} \qquad (8)$$

$$—NH_2 + —NCO \rightarrow —NH{\cdot}CO{\cdot}NH— \text{(exothermic)} \qquad (9)$$

The initial interaction of phosgene and the mixture of tolylene diamine isomers therefore results in a complex mixture. Dihydrochlorides of the diamine isomers, *e.g.* (5), are precipitated as also are monohydrochlorides containing isocyanate (6) and carbamoyl chloride groups (7). Substituted ureas (8) are formed in

(5)   (6)   (7)

(8)
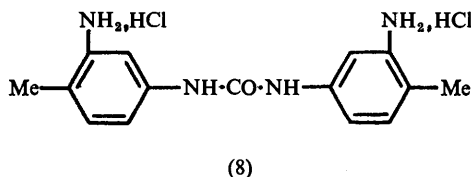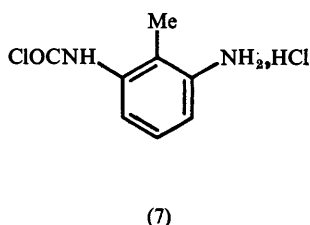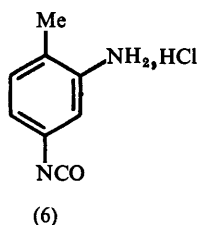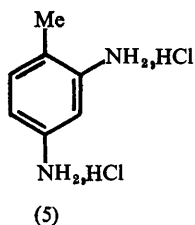
consequence of reaction (9), an undesirable one referred to later. Ureas constitute loss of yield and their formation is minimized by working in dilute solution using a large excess of phosgene, and having efficient agitation in the reactor.

Reactions taking place in the second-stage reactor. An excess of phosgene is used in the first-stage reactor in order to minimize the formation of substituted ureas (reaction 9). The temperature attained in this reactor is therefore limited, unless it is operated at super-atmospheric pressure. The precipitated suspension obtained in the first-stage reactor flows continuously to a second-stage reactor maintained at a higher temperature (80—120 °C). The bulk of the excess phosgene here evaporates and is evolved together with hydrogen chloride which results from dissociation of carbamoyl chlorides (reaction 7). The amine hydrochlorides precipitated at the first stage react in the following manner:

$$—NH_2HCl + COCl_2 \rightarrow —NHCOCl + HCl \qquad (10)$$

This reaction, which has not been closely studied, probably requires initial dissociation of the salt to free amine and hydrogen chloride. The overall reaction involves a heterogenous phase, the precipitated mixed amine hydrochlorides, and it is important to obtain this material in a finely divided form in order that it may react rapidly in the second reactor. If this does not happen third and fourth hot stage reactors will be required to complete the reaction. It is more difficult to obtain the mixed hydrochlorides in a dispersed form in the process in which the diamine is contacted first with hydrogen chloride to form the salt. This makes the overall process more prolonged than in direct phosgenation. Much attention has been given to the study of mixing conditions in the first-stage reactor in order to obtain finely divided precipitates as well as to minimize formation of substituted urea. Many patents claiming improved procedures have been filed and reference is made to typical processes.[14]

The concentration of phosgene in the hot stage reactors is relatively low, while the concentration of isocyanate is high because of the dissociation of carbamoyl chlorides; it is considered that additional formation of substituted ureas occurs as a result of the following overall reaction which competes with reaction (10).

$$-NH_2,HCl + -NCO \rightarrow -NH \cdot CO \cdot NH- + HCl \qquad (11)$$

The formation and further reactions of substituted ureas. In addition to the substituted linear ureas of type (8) formed in consequence of reactions (9) and (11) a cyclic type of urea, methylbenzimidazolone (4), is also produced at the initial mixing stage when the tolylene 2,3- and 3,4-diamine isomers react with phosgene:


(4)
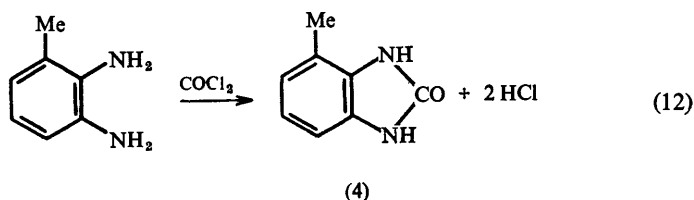
Scheme 2

All ureas, whether substituted linear ones or cyclic methylbenzimidazolones, are undesirable because their presence results in loss of yield and leads to impurities in the final product. In addition to the direct loss of yield resulting from reaction of an amine group with an isocyanate group to form a urea, further loss occurs because the hydrogen atoms in both linear and cyclic ureas are reactive to isocyanate and combination to form substituted biurets (9), triurets (10), and higher polyurets (reaction 13) can take place. The presence of small amounts of compounds containing reactive —NH— groups can therefore lead to disproportionate losses of yield.

[14] Bayer, B.P. 761 590; ICI, B.P. 1 034 285; Bayer, Ger. P. DT 2 153 268.
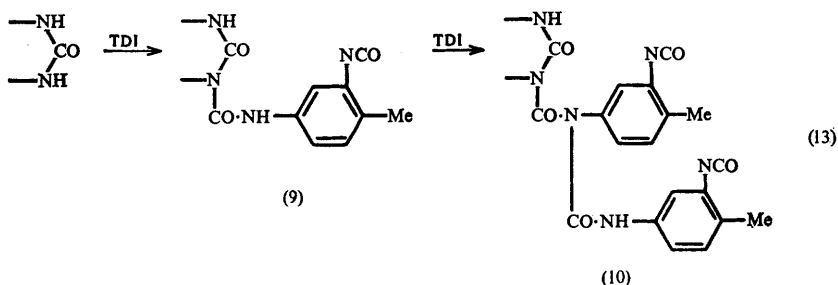
Scheme 3

Compounds containing the stable isocyanurate ring (11), *cf.* the trimer of TDI (1), are present in the reactor mixture. Increased amounts form during concentration and distillation. It is considered that these may result from ring closure of the higher polyurets.


(14)
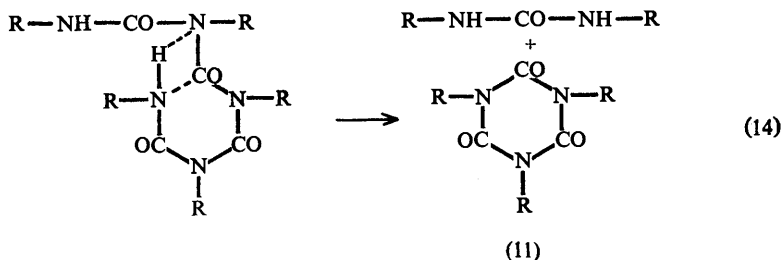
Scheme 4

This type of mechanism would explain the known observation that heating a monoisocyanate with a small amount of a compound containing active hydrogen may polymerize virtually all the isocyanate present.

Substituted aromatic ureas react readily with phosgene. By analogy with the aliphatic series,[15] it is considered that thermally unstable substituted allophanoyl chlorides (12) and substituted chloroformamidines (13) are first formed. The former can eliminate hydrogen chloride to form isocyanate, although available evidence indicates that this reaction takes place only to a limited extent during the production of TDI. The chloroformamidines appear to react with additional phosgene to give a substituted chloroformamidine-*N*-carbonyl chloride (14) the presence of which can be demonstrated[16] in the phosgenation products of the linear urea (8). It has also been shown[16] that, under the catalytic influence of hydrogen chloride, the chloroformamidine-*N*-carbonyl chlorides decompose by two routes to yield substituted carbodi-imides (15) and substituted isocyanide

[15] H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *J. Org. Chem.*, 1964, **29**, 2401.
[16] R. P. Redman, private communication.

dichlorides (16). The latter have boiling points close to the analogous isocyanates and are not readily separated by distillation. These compounds, although present in small amounts, therefore contribute to persistent chlorine-containing impurities in the final product.
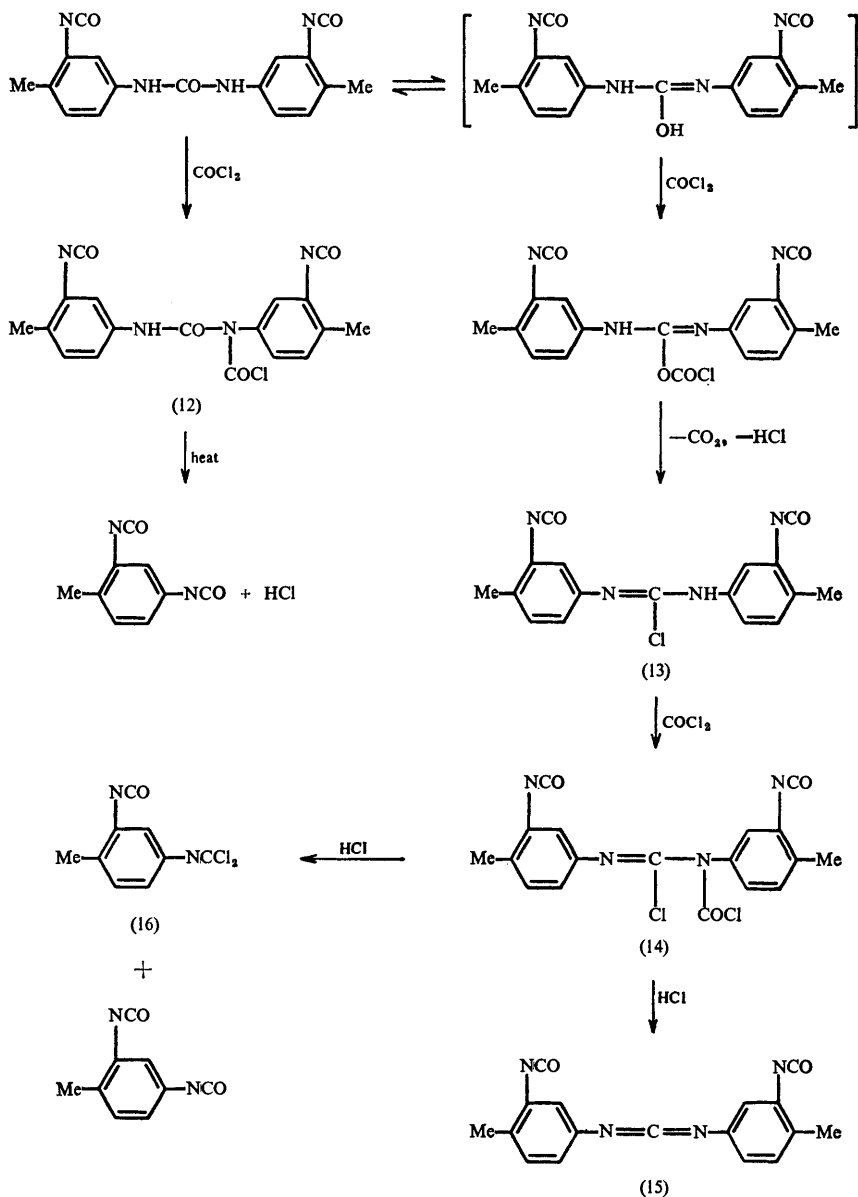

Scheme 5

The cyclopolymerization of 2,3- *and* 3,4-*tolylene di-isocyanates.* Although *ortho*-diamines react with phosgene mainly to form cyclic ureas, it has been found that the 2,3- and 3,4-isomers of tolylene diamine can react with phosgene to give low yields of the corresponding *ortho*-di-isocyanates (17). The formation of these compounds has been studied by Schnabel and Kober[17] who have suggested the mechanism shown.
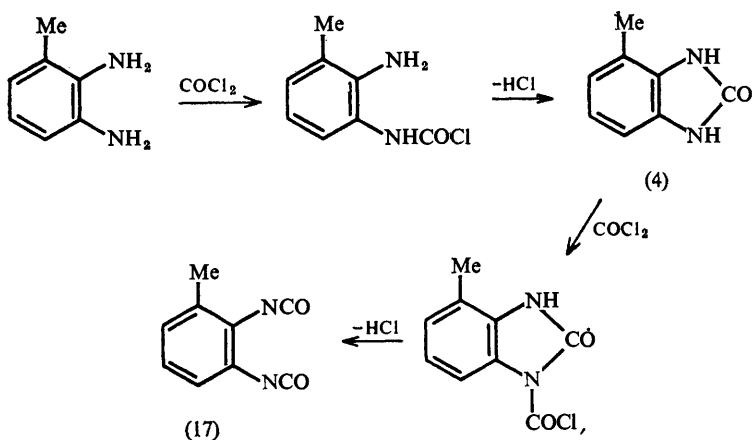
Scheme 6

The presence of the *ortho*-di-isocyanates as impurities in the mixed 2,4- and 2,6-tolylene di-isocyanates used commercially can give rise to undesirable turbidity. This is the result of spontaneous cyclopolymerization to (18), which is particularly insoluble.

(18)
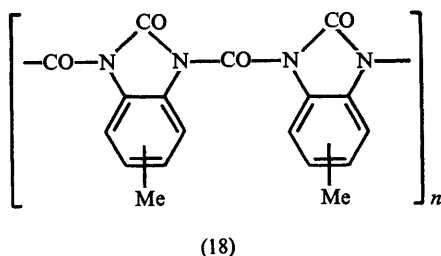
Manufacturers take steps to limit the presence of *ortho*-di-isocyanates in their products. The best solution is to remove *ortho*-isomers from the tolylene diamine

[17] W. J. Schnabel and E. Kober, *J. Org. Chem.*, 1969, **34**, 1162.

before phosgenation. The formation of cyclopolymers, including those from *ortho*-di-isocyanates, has recently been reviewed.[18]

Distillation of tolylene di-isocyanate. After phosgenation, tolylene di-isocyanate must be recovered in a pure form from the dilute crude reactor material. A complicated work-up procedure is necessary because of the reactivity of the di-isocyanates with their own impurities, the linear and cyclic substituted ureas and because of side-reactions which may introduce persistent chlorine-containing impurities. Concentration and distillation by 'batchwise' methods originally used gave poor yields and these operations are now carried out continuously in specialized equipment. Procedures vary according to the solvent employed. Climbing-film and thin-film evaporators[19] are used to separate the di-isocyanate from the involatile but reactive by-products without delay. The residence time of material in evaporators of this nature is of the order of seconds and further reaction of TDI with its impurities is minimized. The distillate from the evaporators is virtually free from impurities containing active hydrogen atoms and can be refined further using conventional fractionating columns.

The commercial product is of high purity; the ratio of 2,4- to 2,6-isomer is strictly controlled and manufacturers usually specify the content of isocyanate and the levels of acidic and chlorine-containing impurities present. TDI is largely used for making flexible foams by reaction with mixtures of water and polyether polyols. Catalysts are used in the foam-making process, and as impurities present in TDI have a deleterious influence on catalytic activity they must be kept at low and consistent levels.

Strict precautions must be taken when handling tolylene di-isocyanate; its vapour irritates the respiratory system and may cause bronchial asthma. After exposure to the vapour individuals may become sensitized and develop acute symptoms on subsequent exposure to minute amounts of the di-isocyanate.

Pure 2,4-tolylene di-isocyanate. Pure 2,4-tolylene di-isocyanate is used industrially in small quantities. It can be obtained from the more important mixture containing 80% 2,4- and 20% 2,6-isomers by freezing, when the pure material, m.p. 19.5—21.5 °C separates. Conditions can be regulated to leave a mixture containing 65% 2,4- and 35% 2,6-isomers, which is used commercially, and can also be made by nitrating toluene to give a mixture of 2- and 4-nitrotoluenes, separating the isomers by distillation, and nitrating the 2-nitrotoluene further to give a *ca.* 65:35 mixture of 2,4- and 2,6-dinitrotoluene. After reduction the mixed diamines are phosgenated to give the corresponding di-isocyanates.

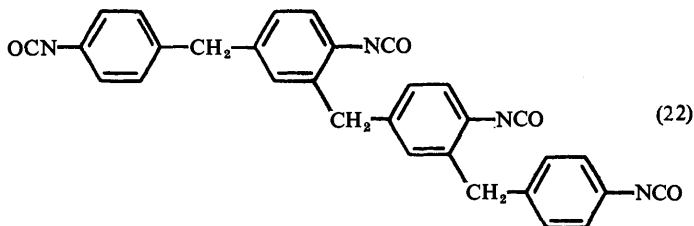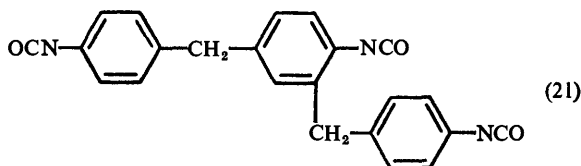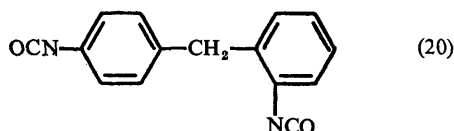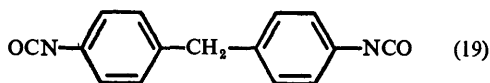**Diphenylmethane Di-isocyanate (MDI).**—Diphenylmethane di-isocyanate (19) is the second most important polyisocyanate in large-scale production. The pure 4,4′-isomer is made as a distilled product but the principal commercial product

[18] G. C. Corfield, *Chem. Soc. Rev.*, 1972, **1**, 523.
[19] 'Encyclopedia of Chemical Process Equipment', ed. W. J. Mead. Reinhold, New York, 1964, pp. 357, 968.

is an undistilled mixture known as 'polymeric MDI' containing about 50%
4,4'-isomer together with higher methylene-bridged polyphenylene polyiso-
cyanates, *e.g.* (21) and (22).

A small amount (5—10%) of the 2,4'-isomer (20) is usually present in marketed
polymeric MDI, but some brands recently introduced contain considerably more
together with significant amounts of the 2,2'-isomer.

$$OCN \text{—} \langle \text{—} \rangle \text{—} CH_2 \text{—} \langle \text{—} \rangle \text{—} NCO \quad (19)$$

$$OCN \text{—} \langle \text{—} \rangle \text{—} CH_2 \text{—} \langle \text{—} \rangle \quad (20)$$
$$NCO$$

$$(21)$$

$$(22)$$

Other polyisocyanates resulting from side-reactions are also present and are
referred to below. The mean functionality of the commercial product is about
2.8, *i.e.* on average each molecule contains 2.8 —NCO groups. Although the
material is a complex mixture, every effort is made during manufacture to
maintain consistent composition to ensure reproducibility in the various poly-
urethane systems in which it is used. The product is analysed for its main iso-
cyanate components as well as for acidic, chlorine-containing, and other
impurities which could upset the polymer-forming reactions if present in
excessive amounts.

The 4,4′-isomer, a colourless solid of low melting point, is treated with polyols to make elastomers, thermoplastic materials, shoe-soling compositions, and elastomeric fibres of the 'Spandex' type. Polymeric MDI, a viscous liquid, is used in large amounts to make rigid polyurethane foam required for heat and sound insulation. A particularly valuable feature of pure and polymeric MDI's is low vapour pressure which makes them less toxic and safer to handle than tolylene di-isocyanate.

Pure 4,4′-MDI is normally isolated from the polymeric MDI mixture of polyisocyanates. The starting material in the manufacture is aniline, which reacts with formaldehyde to give a mixture of isomeric diaminodiphenyl-methanes and higher methylene-bridged polyphenylene polyamines. Two distinct processes are used industrially. In one, a large excess of aniline is heated with formaldehyde under pressure in the presence of a catalyst which may be an acid, a salt, or an acid-activated clay. In the second and more commonly employed process, aniline is treated with defined amounts of formaldehyde and hydrochloric acid in an agitated reactor at relatively low temperature. The hydrochloric acid addition may precede or follow the formaldehyde addition. The reaction mixture is heated to 100 °C to convert intermediate products into primary amines. The reaction of aniline with formaldehyde is exothermic, (-11 kcal mol^{-1} aniline reacted), and a complicated sequence of concurrent and consecutive reactions takes place in both types of process. Many patents describe both catalytic and hydrochloric acid processes and reference is made to typical examples.[20]

Mechanism of the formation of polyamine. The reaction of aniline with formaldehyde was reviewed by Sprung in 1940,[21] and little fundamental work has been published since.[22] In general, investigation has been confined to industrial laboratories. It is now considered[23] that the mechanism of polyamine formation is as outlined below.

When formaldehyde is added to aniline in the presence of acid, the electrophile (23) is produced with the elimination of water:

(23)
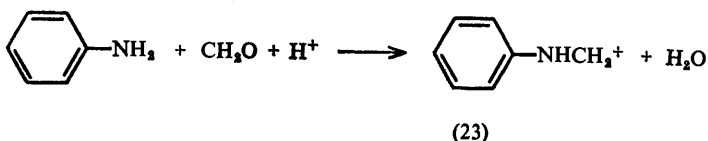
Scheme 7

[20] ICI, B.P. 1 038 266; B.P. 1 229 695; Mobay, B.P. 1 154 980.
[21] M. M. Sprung, *Chem. Rev.*, 1940, **26**, 297.
[22] J. F. Walker, 'Formaldehyde', Reinhold, New York, 1964, p. 369.
[23] R. C. Smith, private communication.

This species then substitutes into an aromatic nucleus to give *p*-aminobenzyl-aniline (24) by reaction with aniline, or higher polymeric species (25) by reaction with either secondary amine, *e.g.* (24) itself or higher analogues already produced. A polymeric secondary amine of type (25) is referred to as poly(aminobenzyl-aniline) or poly(anhydroaminobenzyl alcohol).
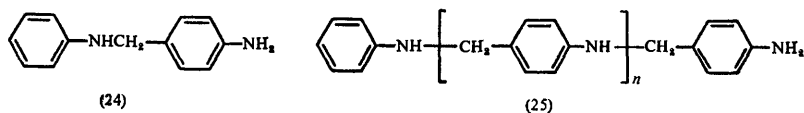
The second stage of the reaction, known as the 'isomerization' stage, converts secondary amine into primary amines. The reaction is, in fact, an intermolecular reaction between a protonated secondary amine and a non-protonated primary amine, so is extremely pH sensitive, and is usually accelerated by heating at 95—100 °C after formaldehyde addition. The 'isomerization' is illustrated here by the reaction between a protonated polymeric secondary amine and aniline to give 4,4'-diaminodiphenylmethane (26) and a lower polymer of the secondary amine.

Scheme 8
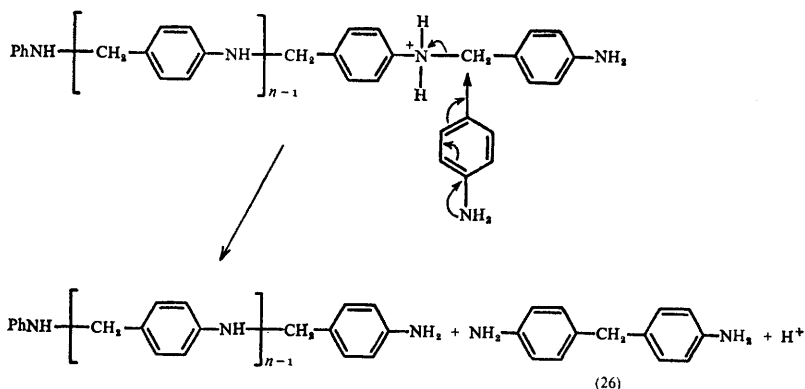
2,4'-Diaminodiphenylmethane (27) is thought to arise from species (23) substituting into an aromatic nucleus *ortho* to the NH_2 group. Triamines, *e.g.* (28), arise from the diamines (26) or (27) taking part in the initial reaction with formaldehyde to give analogues of (23). Higher methylene-bridged polyphenylene polyamines are formed in a similar manner.

Seven isomeric triamines and fifteen isomeric tetra-amines are possible, although a smaller number predominate because of stereoselectivity at the reaction stage.

As the reactions taking place during addition of formaldehyde are exothermic it is important to control the temperature and maintain good mixing in the
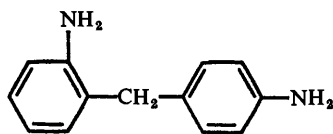
(27)
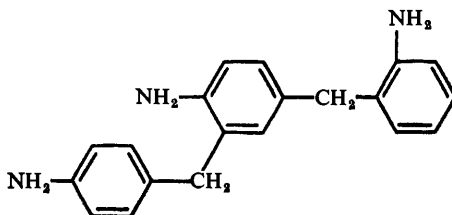
(28)

reactor to avoid undesirable side-reactions occurring as a result of local excesses of formaldehyde or overheating. After addition of formaldehyde is complete the reaction mixture is heated until 'isomerization' of secondary to primary amines is virtually complete.

It will be noted that 'isomerization' depends on the presence of both free aromatic amine and a protonated species. The rate of 'isomerization' is controlled therefore by the ratio of aniline to acid initially used as well as by dilution and temperature. As might be anticipated, the rate of 'isomerization' decreases when the molar ratio of acid to aniline exceeds unity because of the decrease in the concentration of free amine. After the 'isomerization' stage, the reaction mixture is neutralized with caustic soda when the polyamine separates as an oil which is washed free from salt. This operation is usually done continuously in appropriate equipment at a sufficiently high temperature (90—100 °C) to keep the polyamine liquid. The polyamine is next processed to remove water and residual aniline. It is of interest that a considerable amount of aniline does not react even when less than two mol of aniline per mol of formaldehyde is employed. This is the result of the speed with which formaldehyde reacts with diamines to form tri-amines and so on. Methanol, frequently used to stabilize aqueous formaldehyde against polymerization to paraformaldehyde, is recovered from the saline wash-water as a marketable by-product. Recovered aniline is re-used in the process and it is of interest that it contains 2- and 4-toluidine, as well as *N*-methylaniline, formed as impurities during the addition of formaldehyde.

*Composition of the polyamine.*The composition of the polyamine can be varied widely according to the conditions used, the principal factors being ratio of aniline to formaldehyde, ratio of aniline to hydrochloric acid, dilution, tempera-ture, and rate of addition of formaldehyde. Thus large excesses of aniline favour

formation of the 4,4′-diamine (26), whereas small amounts of hydrochloric acid result in higher amounts of the 2,4′-diamine (27) together with larger proportions of the higher methylene-bridged polyamines. The catalysed high-temperature pressure process gives a polyamine containing less 4,4′-diamine and much more of the 2,4′- and 2,2′-isomers than does the aqueous hydrochloric acid route, owing to reduced stereoselectivity at the higher reaction temperatures. Some typical analyses of polyamines are given in Table 1.

Table 1 *Composition of polyamine*

Process	Diamines			Higher
	4,4′-	2,4′-	2,2′-	polyamines
Aqueous HCl	60%	5.0%	trace	35%
Catalytic high temperature	18.3%	18.6%	4.7%	58%

Small amounts of 3-methyldiphenylmethane-4,4′-diamine (29) are often found in the polyamine as well as a little un-isomerized secondary amine and 3-phenyl-3,4-dihydroquinazoline (30). The presence of secondary amine and the quinazoline is undesirable as both give rise to acidic chlorine containing impurities during phosgenation.
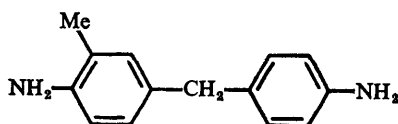
(29)
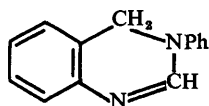
(30)

Phosgenation of the polyamine. The polyamine can be distilled under reduced pressure to give fractions containing the high-boiling diamine and triamine isomers, but normally it is phosgenated directly to the corresponding mixture of polyisocyanates. The equipment and conditions used are similar to those for the continuous phosgenation of tolylene diamine. The same inert solvents, *e.g.* chloro- or dichloro-benzene, are used and the product is obtained as a dilute (5—25%) solution. Some care is necessary in selecting materials of construction for the phosgenation reactors because, although isocyanate solutions containing phosgene and hydrogen chloride are not particularly corrosive to mild or stainless steel, some of the by-products of side-reactions can be. Mixtures of poly-amine-derived ureas and phosgene or hydrogen chloride corrode steel quite

readily, although the iron co-ordination compounds formed have not been studied in any detail. Special grades of stainless steel are normally used to minimize corrosion.

The use of solvent containing small amounts of water or inadequately dried polyamine also leads to corrosion. As the bulk of the product is used as an un-distilled product, corrosion products remain in it. High levels of iron and other transition metals in 'polymeric' MDI are deleterious as the metals have consider-able catalytic activity in the reactions of the polyisocyanate in many polyurethane applications. Variable contents in particular are undesirable as they lead to inconsistency in the production of derived urethane polymers.

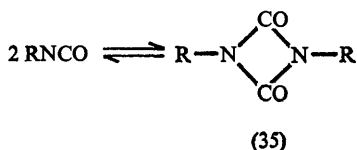*Reactions taking place during phosgenation.* The reactions taking place during the phosgenation of the polyamine are even more difficult to study than those occurring with tolylene diamine because of the greater complexity of the amino-compounds involved. In general, the main reactions appear to follow the pattern of reactions (5)—(11) described above for tolylene diamine. The reaction taking place in the first-stage reactor has a similar order of exotherm and the suspension which flows from this reactor appears to be highly solvated with phosgene and less crystalline than in the case of tolylene diamine. It reacts more readily at the second, hot stage. This is attributed to the greater complexity of the polyamine mixture giving a precipitate of smaller particle size. Linear ureas (reaction 9) appear to be formed and there is evidence that these react with isocyanate groups to form biurets and polyurets (see reaction 13) and with phosgene to form *N*-carbonyl chlorides [*cf.* (13)]. A secondary amine, *e.g.* (24), reacts with phos-gene to give a secondary carbamoyl chloride (31) which cannot dissociate in the manner of a primary carbamoyl chloride and remains as a chlorine-containing impurity. 3-Phenyl-3,4-dihydroquinazoline (30) reacts with hydrogen chloride to give a stable hydrochloride which also remains in the product.
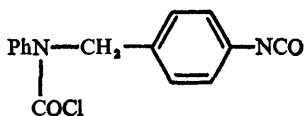
(31)

In some respects, control of side reactions is of greater importance than in production of tolylene di-isocyanate as polymeric MDI is not distilled and impurities remain as contaminants.

Concentration of dilute polymeric MDI. As in the case of tolylene di-isocyanate, the solvent is removed from dilute polymeric MDI without delay. Any reaction of isocyanate groups with impurities such as substituted ureas containing active hydrogen atoms is minimized by using climbing-film and thin-film evaporators

having low hold-up times, for continuous concentration. The polymeric MDI produced contains appreciable amounts of chlorine-containing impurities, and it is necessary to eliminate these to some extent to make the material usable for polyurethane applications. This is done by a short treatment at high temperature under specialized conditions.[24] Phosgene and hydrogen chloride are evolved during the treatment and it is considered that one of the reactions involves decomposition of a chloroformamidine-*N*-carbonyl chloride (32), formed as a result of phosgenation of urea groups, to a substituted carbodi-imide (33). On cooling,

$$-NH-CO-NH- \xrightarrow{\text{COCl}_2} -N=C-N- \xrightarrow{\text{heat}} -N=C=N- + COCl_2$$

$$\underset{\text{Cl}\quad\text{COCl}}{\mid\quad\mid}$$

$$(32) \qquad\qquad (33)$$

carbodi-imide groups reversibly combine with isocyanate groups to form substituted uretonimines (34), the presence of which in polymeric MDI at low temperature results in a viscosity increase in consequence of the increase in molecular complexity.

$$-N=C=N- + -NCO \rightleftharpoons$$

(33)

(34)

Scheme 9

Yet another reaction occurring as the result of the heat treatment process concerns the formation of an insoluble sediment arising from the dimerization of isocyanate groups.

Dimerization of isocyanates. Many aromatic isocyanates can be dimerized[25] to substituted uretediones (35); the reaction is reversible and in fact it is the dimer which is thermodynamically stable at room temperature, although its rate of formation at this temperature in the absence of suitable catalysts (*e.g.* trialkylphosphines or 4-dimethylaminopyridine) is very slow. The sediment which forms

[24] ICI, B.P. 1 080 717; du Pont, B.P. 1 015 977.
[25] R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, 1957, **57**, 54.

$$2\,RNCO \rightleftharpoons R-N\underset{\underset{CO}{\diagup}}{\overset{\overset{CO}{\diagdown}}{\diagup}}N-R$$

(35)

Scheme 10

both in polymeric MDI and the pure 4,4′-MDI comprises mainly the very insoluble compound (36).

$$OCN-\text{⟨⟩}-CH_2-\text{⟨⟩}-N\underset{\underset{CO}{\diagup}}{\overset{\overset{CO}{\diagdown}}{\diagup}}N-\text{⟨⟩}-CH_2-\text{⟨⟩}-NCO$$

(36)
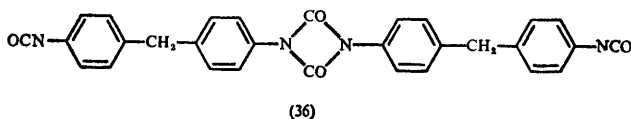
At 200 °C, dissociation of the uretedione to 4,4′-MDI is virtually complete; at 120 °C the equilibrium mixture contains 6.3% dimer. If, after concentration and heat treatment, polymeric MDI is allowed to cool slowly as it may do in bulk, appreciable amounts of uretedione form and are precipitated as sediment. It is therefore necessary to heat polymeric MDI to around 200 °C and then cool rapidly to freeze the equilibrium and so prevent deposition of sediment.

Dimer forms slowly in polymeric MDI on prolonged storage and also in pure 4,4′-MDI in the crystalline state. For this reason the latter is sometimes kept in refrigerated storage. In spite of its sterically unhindered 4′-isocyanate group, 2,4′-MDI does not dimerize readily.

Pure 4,4′-diphenylmethane di-isocyanate. Technically pure 4,4′-diphenylmethane di-isocyanate is obtained by distillation or crystallization of polymeric MDI. Many variations of these basic processes have been patented. As the presence of quite small amounts of the 2,4′-isomer can have a detrimental effect on derived elastomers, a polymeric MDI precursor is made by phosgenating a polyamine containing a low content of 2,4′-diamine and a high proportion of the 4,4′-isomer. This type of polyamine can be obtained by treating a large excess of aniline with formaldehyde in the presence of approximately equimolecular proportions of hydrochloric acid and aniline. After phosgenation, polymeric MDI containing corresponding proportions of 2,4′- and 4,4′-MDI is obtained.

A fraction rich in 4,4′-MDI, obtained by distillation or crystallization, is usually purified further to remove chlorine-containing impurities and residual 2,4′-isomer by re-distillation or re-crystallization or by a combination of these methods. The boiling point of 4,4′-MDI is high (156—158 °C at 0.1 mmHg) and, like tolylene di-isocyanate, it must be distilled in specialized thin-film evaporators

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capable of operating at low pressures and having short hold-up times if undue degradation is to be avoided.

To achieve a currently viable process it is essential to use the undistilled or uncrystallized residues from the polymeric MDI precursor. The composition of the original polyamine, and hence the polymeric MDI precursor and the proportion of 4,4'-MDI removed, are therefore arranged so that the composition of the residue is similar to the product normally used for making polyurethane foams. Typical analyses of the precursor, technically pure 4,4'-MDI, and polymeric MDI residue are given in Table 2.

Table 2 *Composition of pure and polymeric diphenylmethane di-isocyanate*

Material	Diphenylmethane di-isocyanate		Tri-isocyanates	Higher poly-isocyanates
	4,4'-	2,4'-		
Precursor	65%	4.0%	20%	11%
Pure MDI	98%	2.0%	nil	nil
Polymeric MDI residue	56%	4.4%	25%	13.7%

Technically pure 4,4'-diphenylmethane di-isocyanate is a solid, m.p. 38—39 °C. A liquefied product, also used commercially, is obtained by converting a small proportion of the isocyanate groups into carbodi-imide. This can be done by heating alone,[26] but is usually achieved by heating in the presence of a catalytic phosphorus compound such as a trialkyl phosphate.[27] The most effective catalysts known are the phospholine oxides,[28] *e.g.* the 3-methyl-1-ethyl or 3-methyl-1-phenyl derivatives (37), which convert isocyanates into the corresponding carbodi-
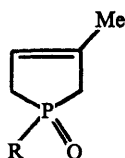
(37) R = Et or Ph

imides at room temperature. A mechanism for the catalytic action of these oxides has been proposed.[29]

The use of titanium and other metal alkoxides as catalysts for carbodi-imide formation has been patented.[30]

[26] Bayer, B.P. 899 036.
[27] Upjohn, B.P. 1 069 858.
[28] du Pont, U.S.P. 2 853 473.
[29] J. J. Monagle and J. V Mengenhauser, *J Org. Chem.*, 1966, **31**, 2321.
[30] du Pont, U.S.P. 3 426 025.

On cooling, the carbodi-imides associate with isocyanate groups to form substituted uretonimines [see (34)].

4 The Cyanation and Carbonylation Processes for Making Isocyanates

The large number of patents issued shows that several companies have closely examined the possibilities of the cyanation and carbonylation processes as alternatives to phosgenation of primary amines for manufacturing isocyanates.

The cyanation process, in which an alkyl or aralkyl chloride, sulphate, or phosphate is treated with a metal cyanate was used by Wurtz[31] to synthesize the first organic isocyanate:

$$RCl + NaCNO \rightarrow RNCO + NaCl$$
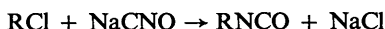
Numerous patents have been granted claiming the making of alkyl and aralkyl mono- and poly-isocyanates. Particular attention has been given to the treatment of bis(chloromethyl) derivatives of benzene and xylene with sodium cyanate to obtain polyisocyanates comparable in cost with tolylene di-isocyanate but capable of giving urethane polymers less subject to discoloration. The heterogeneous reaction with finely ground sodium cyanate is not easy to control, however, and considerable amounts of substituted isocyanurates (39) are usually formed as by-products, as well as the di-isocyanate (38). A typical process[32] has been patented by the Marathon Oil Co.
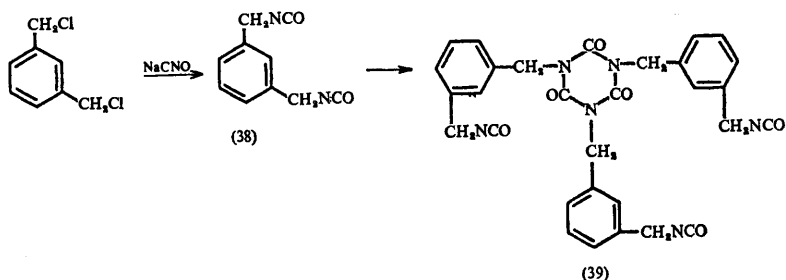
Scheme 11

Bayer[33] claims a similar process for making methoxymethyl isocyanate (40).

$$MeOCH_2Cl + NaCNO \rightarrow MeOCH_2NCO + NaCl$$
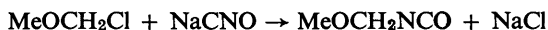
(40)

Sodium cyanate is much dearer to produce than phosgene and adds to the expense of the process, while unchanged chloro-compounds are sometimes

[31] A. Wurtz, *Compt. rend.*, 1848, **27**, 241; *Annalen*, 1849, **71**, 326.
[32] Marathon Oil Co., U.S.P. 3 458 448.
[33] Bayer, B.P. 1 104 917.

difficult to separate from derived isocyanates because of the closeness of their boiling points.

Many of the reactive chlorine compounds which have been used for cyanation are most readily obtained by chloromethylation of aromatic compounds. A hitherto unsuspected hazard concerning this reaction has recently been reported.[34] Bis(chloromethyl)ether, a by-product and/or an intermediate in chloromethylation has been found to be a potent carcinogen as well as an acute lung irritant and it is recommended that this reaction be avoided.

Cyanation is not seen at present as a feasible route for manufacturing other than very specialized isocyanates.

In the carbonylation process an aromatic nitro-compound is converted directly into an isocyanate on treatment with carbon monoxide. The process is potentially attractive for making tolylene di-isocyanate, as the intermediate stage of reducing dinitrotoluene to the diamine is eliminated. The direct use of carbon monoxide also avoids initial treatment with chlorine to obtain phosgene and the subsequent excess production of hydrogen chloride. The process has been examined by several manufacturers and numerous patents have been published by American Cyanamid, Shell, ICI, and Olin Mathieson.

The first direct synthesis of an isocyanate by carbonylation was claimed by Hardy and Bennett[35] of American Cyanamid, who obtained a 35% yield of phenyl isocyanate by treating nitrobenzene with carbon monoxide and a palladium or rhodium on alumina catalyst in the presence of a Lewis acid.

A 57% yield of tolylene di-isocyanate from dinitrotoluene is claimed in a patent by Olin Mathieson[36] using a mixture of palladium, molybdenum, iron, and chromium catalysts, while Shell claim 70—76% yields using a mixed palladium, iron, and molybdenum catalyst in the presence of pyridine.[37]

Expensive rare-metal catalysts seem to be essential for the carbonylation synthesis of isocyanates. As far as is known, no large-scale plant operating this type of process has been commissioned although patents continue to appear.

[34] 'Organic Reactions', Wiley, New York, 1972, Vo.l19, p. 422.
[35] W. B. Hardy and R. P. Bennett, *Tetrahedron Letters*, 1967, 961.
[36] Olin Mathieson, B.P. 1 252 517.
[37] Shell, U.S.P. 3 719 699.