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(54) PRODUCTION OF ISOCYANATES FROM ESTERS OF CARBAMIC ACIDS

(71) We, ATLANTIC RICHFIELD COMPANY, a corporation organised under the laws of the State of Pennsylvania, United States of America, of ARCO Plaza, 515 S. Flower Street, Los Angeles, State of California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of isocyanates from esters of carbamic acids, otherwise known as urethanes.

The conversion of esters of carbamic acids to the corresponding isocyanate and alcohol has been extensively investigated. An early Patent United States No. 2,409,712 (1946) shows the pyrolysis of N-substituted carbamic esters in the liquid phase at subatmospheric pressures to give the isocyanate and alcohol. Thus ethoxyethoxyethyl N - lauryl carbamate was pyrolyzed in the liquid phase at 210°C to 230°C under high vacuum, i.e. 2 mm. Hg pressure (no time given) to give lauryl isocyanate and ethoxyethoxyethanol. The yield of isocyanate was 75 per cent. The use of such a high vacuum, however, poses problems in commercializing such a process and consequently it is not believed to have been commercialized. Other examples showed much lower yields down to 37 per cent.

In an article in the Journal of the American Chemical Society, Vol. 80, page 5495 et seq. (1958), Dyer et al report that monomeric carbamates of the type RNHCOOR' are known to be degraded above 200°C to the isocyanate and alcohol. The authors show, however, that biscarbamates prepared from methylenebis - (4 - phenyl isocyanate) and 1 - butanol, 2,2 - dimethyl - 1 - propanol and benzyl alcohol and the polycarbamate

from methylene - bis(4 - phenyl isocyanate) and 1,6 - hexane diol when pyrolyzed at 300°C produced carbon dioxide and the parent alcohol or diol and also yielded amine residues from the benzyl carbamate and polycarbamate.

In another article in the Journal of the American Chemical Society, Vol. 81, page 2138 et seq. (1959) Dyer et al show that ethyl carbanilate gave phenyl isocyanate (60—75 mole per cent based on carbanilate degraded, 44—30 per cent degraded, in 6 hours and 4 hours, respectively) and the alcohol when heated at 200°C under pressure sufficiently low 60—120 mm. Hg to vaporize the alcohol but high enough to retain the isocyanate. Thus even under these conditions other products were formed. At atmospheric pressure no phenylisocyanate was obtained, although 70 per cent of the ethyl carbanilate was destroyed. At 250°C and atmospheric pressure alpha - methylbenzyl carbanilate gave major amounts of aniline, alpha - methylbenzyl aniline, styrene and carbon dioxide.

Dicarbamates such as bis (2 - acetoxyethyl) 1,6 - hexane dicarbamate according to United States Patent 3,054,819 (1962) can be distilled in the presence of a basic catalyst such as tribenzylamine at low pressures, for example, 6 mm. Hg at 215°C to 260°C to produce the hexamethylene diisocyanate at a yield of 40 per cent. Without the catalyst a yield of only 17 per cent was obtained.

A more recent British Patent No. 1,247,451 (1971) discloses that it was known that organic isocyanates can be produced by the non-catalytic pyrolysis of urethanes at temperatures above 250°C but the yield is undesirably low, and if lower temperatures are employed the isocyanate and alcohol will react to reform the original urethane. This confirms the findings discussed hereinbefore wherein various expedients such as catalysts

and low pressures were employed with specific carbamates. The aforementioned British Patent proposes to pyrolyze diethyl toluene - 2,4 - dicarbamate in the presence of a Lewis acid such as ferric chloride catalyst to produce toluene - 2,4 - diisocyanate (TDI). A yield of approximately 59 mole per cent is shown. In general, the reaction is carried out at from 400°C to 600°C in the presence of the catalyst at subatmospheric pressures to form vapors, and condensing the vapors to recover the organic isocyanate product.

Thus although the monocarbamates can be noncatalytically pyrolyzed to the monoisocyanate and alcohol employing high temperatures and low pressures the yields are undesirably low. Likewise certain dicarbamates have been pyrolyzed to the diisocyanate and alcohol but the yields have generally been unsatisfactory for commercial purposes; moreover, in most cases the decomposition products are predominantly amines and carbon dioxide, not the desired diisocyanate. The aforementioned British Patent also requires high temperatures and low pressures and in addition a Lewis acid catalyst such as ferric chloride which renders such process highly undesirable from a commercial viewpoint because of the highly corrosive nature of such acids.

The present invention obviates these problems and others encountered by the above illustrated prior processes. It can be carried out at atmospheric, subatmospheric or super-atmospheric pressures. The present invention also does not require the use of catalysts and gives extremely high yields of the isocyanate and alcohol. It can be used with esters of carbamic acids in general, but is particularly useful for the production of the mono- and diisocyanates from their corresponding esters of mono- and dicarbamic acids.

According to this invention a method is provided for producing isocyanates from carbamates which comprises thermally treating the carbamate in an inert organic solvent for the carbamate.

In accordance with the invention, there is provided a method for the production of isocyanates from esters of carbamic acids having the formula



or



wherein each R is a substituted or unsubstituted mono- di or trivalent organic radical selected from saturated and monoolefinic unsaturated straight and branched chain aliphatic and cycloaliphatic radicals containing not more than 32 carbon atoms, alkoxyalkyl radicals having not more than 32 carbon

atoms, and aryl radicals aralkyl radicals and alkaryl radicals containing 1 to 5 rings; each R' is substituted or unsubstituted mono-, di or trivalent radical selected from saturated and monoolefinic unsaturated straight and branched chain aliphatic and cycloaliphatic radicals containing not more than 32 carbon atoms, alkoxyalkyl radicals having not more than 32 carbon atoms, and aryl radicals aralkyl radicals and alkaryl radicals containing 1 to 3 rings; and x is 1, 2 or 3, each R or R' being the same or different, respectively, where x is 2 or 3, said method comprising thermally decomposing said ester at a temperature in the range of from 175°C to 350°C while said ester is dissolved in an inert solvent to produce the isocyanate and alcohol, and separately recovering said isocyanate and alcohol; said solvent being characterized as a compound or mixture of compounds which is (a) a solvent for said ester, (b) liquid and stable at said decomposition temperature and (c) non-reactive with said isocyanate produced in said thermal decomposition reaction, and selected from aliphatic hydrocarbons having from 4 to 32 carbon atoms, halo- and mono-nitro substituted derivatives of said aliphatic hydrocarbons, cyclo aliphatic hydrocarbons, aromatic hydrocarbons having from 1 to 3 rings, alkyl benzenes having from 1 to 15 carbon atoms in the alkyl group, halo- and mono-nitro substituted derivatives of said aromatic hydrocarbons and alkylbenzenes, oxygenated compounds containing from 4 to 32 carbon atoms and selected from ethers, ketones and esters of organic carboxylic acids, and sulfur analogues of said oxygenated compounds.

Although esters of carbamic acids or carbamates are generally referred to as "urethanes" in the literature, the esters are usually individually named as a particular carbamate. The decomposition reaction produces the corresponding isocyanate and alcohol. If the alcohol is lower boiling it can be removed by the use of reduced pressure, by refluxing to distill it overhead or by employing an inert gas to sweep it from the reaction mixture. Conversely, if the alcohol is higher boiling than the isocyanate, the isocyanate can be separated overhead. Alternatively, both the alcohol and isocyanate can be vaporized and separated, for example, by fractionation in the vapor phase.

Preferably R will be an organic aliphatic radical containing up to 18 carbon atoms for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, neopentyl, the hexyls, the heptyls, the octyls, the nonyls, the decyls, the octadecyl, and the monoolefinic compounds such as propenyl, butenyl, pentenyl, hexenyl, decenyl and octadecenyl radicals. The divalent radicals such as ethylene, propylene, butylene, amylene, hexylene, heptylene, octylene, nonylene, decylene and

likewise up to octadecylene also are included and likewise the trivalent radicals. These radicals may be hydrocarbyl or may be substituted with groups non-reactive with isocyanates, for example, nitro or halo, in particular chloro groups. Also included are the cycloaliphatic radicals containing from 5 to 7 carbon atoms preferably such as the cyclopentyl, cyclohexyl and cycloheptyl radicals, likewise the di- and trivalent corresponding radicals. The mono-unsaturated C₅ to C₇ cycloaliphatic radicals are also included as well as the substituted compounds wherein the substituent is an alkyl radical of 1 to 4 carbon atoms, or nitro, or halo such as chloro. The alkoxyalkyl radicals can range from the short chain such as methoxymethyl and ethoxyethyl to the longer chain radicals such as ethoxyethoxyethyl, propoxypropyl, butoxybutyl and may contain up to 18 carbon atoms.

Likewise R can be an aryl radical such as the mono-, di- and trivalent radicals of benzene, toluene, naphthalene, diphenyl, anthracene, phenanthrene, terphenyl, naphthacene, and pentacene with the mono- and divalent radicals being particularly preferred. These aryl radicals can also be substituted with one or more alkyl groups having from 1 to 4 carbon atoms or by radicals non-reactive with isocyanates such as nitro or halo, particularly chloro radicals. In addition to the alkaryl radicals, the aralkyl radicals, such as methyl, ethyl, propyl, and butyl radicals having a hydrogen substituted by phenyl, naphthyl, anthryl or phenanthryl radicals thus the lowest member of the group is methyl having a phenyl radical substituted for a hydrogen on the methyl giving a benzyl radical. Likewise more than one hydrogen may be substituted with a phenyl group as in diphenyl methane, the corresponding aralkyl radical being diphenylmethyl.

Preferably the R' of the above formula will be an organic radical containing up to 18 carbon atoms, i.e. the same alkyl radicals enumerated above for R, the same mono-olefinic compounds enumerated for R the same alkoxyalkyl radicals enumerated for R and the same aryl radicals up to 3 rings enumerated for R.

Representative esters of carbamic acids as characterized above include ethyl phenylcarbamate (alternatively named ethyl N-phenylcarbamate or also the ethyl ester of carbamyllic acid, or preferably ethyl carbanilate), butyl carbanilate, pentyl carbanilate, hexyl carbanilate, octyl carbanilate, ethylene dicarbanilate, 1,3 - propylene dicarbanilate, 1,4 - butylene dicarbanilate, 1,5 - amylene dicarbanilate, 1,6 - hexylene dicarbanilate, 1,8 - octylene dicarbanilate, 1,10 - decylene dicarbanilate, glyceryl tricarbanilate, ethyl 1-naphthalenecarbamate, ethyl 1 - anthracenecarbamate, ethyl 2 - anthracenecarbamate,

ethyl 9 - anthracenecarbamate, diethyl 9,10-anthracenedicarbamate, diethyl 1,5 - anthracenedicarbamate, diethyl 5,6 - naphthacenedicarbamate, diethyl 6,13 - pentacenedicarbamate, ethyl *para* - phenylcarbanilate, ethylene bis(*para* - phenylcarbanilate), diethyl *meta*-benzenedicarbamate, diethyl 1,5 - naphthalenedicarbamate, methyl isopropylcarbamate, ethyl (methoxymethyl) carbamate, methyl sec-butylcarbamate, ethyl(3 - chloropropyl)carbamate, methyl tertiary butylcarbamate, ethyl tert - octylcarbamate, diethyl tetramethylenedicarbamate, ethyl 1 - ethyl - cyclohexanecarbamate, propyl (5,5 - dimethylhexyl) carbamate, methyl *para* - toluenecarbamate, ethyl *para* - (trifluoromethyl) carbanilate, isopropyl *meta* - chlorocarbanilate, ethyl 2 - methyl - 5 - nitrocarbanilate, ethyl 4 - methyl - 3 - nitro - carbanilate, diethyl 4,4 - methylenedicarbanilate, dimethyl *meta* - benzenedicarbamate, dimethyl toluene - 2,4 - dicarbamate, diethyl toluene - 2,4 - dicarbamate, dipropyl toluene - 2,4 - dicarbamate, diisopropyl toluene 2,4 - dicarbamate, dibutyl toluene - 2,4 - dicarbamate, diamyl toluene - 2,4 - dicarbamate, dihexyl toluene - 2,4 - dicarbamate, diphenyl toluene - 2,4 - dicarbamate, di(phenylmethyl)toluene - 2,4 - dicarbamate, dinaphthyl toluene - 2,4 - dicarbamate, di(ethoxyethyl)toluene - 2,4 - dicarbamate, the corresponding esters of toluene - 2,6-dicarbamate, diethyl 4 - chloro - *meta* - benzenedicarbamate, methyl *para* - butoxy carbanilate, ethyl *para* - acetylcarbanilate, ethyl *para* - bromocarbanilate, ethyl *ortho*-nitrocarbanilate, isopropyl *meta* - (trifluoromethyl)carbanilate and triethyl 1,3,5 - benzenetricarbamate. These esters specifically named are obviously merely representative of the very large numbers of esters falling within the definition of the general formula for the compounds which can be converted to isocyanates by the method of this invention. In general, the methyl and ethyl esters are more readily available and therefore these are more preferred.

In carrying out the process of this invention the ester is added to a solvent, to be characterized completely hereinafter in an amount such that substantially all of the ester will be completely dissolved at the reaction temperature. The ester can either be added to the cold solvent and the mixture heated to reaction temperature, which method is generally employed in smaller scale batch runs, or the ester can be added to the heated solvent continuously, as would be more feasible for commercial large scale operations.

The process can be carried out at temperatures ranging from 175°C to 350°C with a more preferred range being from 200°C to 300°C.

The reaction time can vary from several minutes to several hours depending upon the particular ester of the carbamic acid being

reacted and the reaction temperature employed. In general, times ranging from 5 minutes to 4—6 hours are sufficient to obtain the desired objectives of this invention in batch runs, while in continuous runs, residence times of from 10 to 20 hours are preferred.

The process is preferably carried out at atmospheric pressure when suitable high boiling solvents are employed, or it can be run at superatmospheric pressures when lower boiling solvents are used. Subatmospheric pressures can also be used with high boiling solvents but these subatmospheric pressures are not required for the reasons as set forth in the prior art wherein no solvents were used.

It is important in carrying out the process of this invention that the ester of the carbamic acid be substantially completely dissolved in the solvent at reaction temperatures during conversion to the isocyanate and alcohol. If the alcohol is lower boiling than the isocyanate as most frequently is the case, then the alcohol can either be distilled from the solvent as formed or by being removed by the assistance of an inert gas being passed through the solution such as through a fritted disc or similar means for dispersion or by the use of a lower boiling solvent meeting the same criteria as will be set forth hereinafter and boiling between the isocyanate and alcohol. By this means recombination of the alcohol and isocyanate is prevented. Moreover, since the reaction is carried out in solution the formation of polymerization products such as tars and resins is avoided as well as inhibiting the formation of undesirable by-products such as amines and carbon dioxide formerly associated with the thermal decomposition of esters of carbamic acids.

Alternatively if the alcohol is higher boiling than the generated isocyanate, the isocyanate can be removed overhead again by distillation or by the use of an inert gas or by the use of a suitable solvent also to be defined.

In a somewhat more sophisticated alternative which is preferred for continuous operation both the alcohol and isocyanate after formation in the solution are removed into the vapor phase either by the use of an inert gas or a suitable solvent. The isocyanate and alcohol are then separated by suitable fractionation and/or partial condensation. When a solvent is employed to carry the products overhead, it can be used to assist in the condensation of either the isocyanate or alcohol.

The inert gases which can be employed include nitrogen, helium, argon, carbon dioxide, methane, ethane and propane either alone or in mixtures. Nitrogen is preferred because of its convenience.

The solvents which can be used in the process of this invention both in the reaction

medium and for carrying the products overhead are compounds which meet certain criteria. The reaction medium solvent must be capable of dissolving the particular ester of the carbamic acid at reaction temperature to an extent sufficient to make the process practical. Thus if the ester were soluble in the reaction medium solvent to the extent of 1 weight per cent or less the process would be operable, but not particularly attractive from a commercial standpoint. Consequently, although the lower ester concentration limit might be considered to be about 1 weight per cent, it is preferred that the ester be soluble at least to from 3 to 5 weight per cent at reaction temperatures.

Since it is necessary in accordance with the objects of this invention to carry out the conversion of the ester of the carbamic acid in solution it is preferred that the concentration of the ester in the reaction medium solvent should not exceed from 70—80 weight per cent based on the weight of the solution.

Both the reaction medium solvent and the solvent employed to carry the reaction product or products overhead (the carrier solvent) must not decompose at the reaction temperature employed and in addition these solvents cannot contain active hydrogens which, of course, would react with the isocyanate produced. In general any compound containing reactive groups that combine with the isocyanate should not be employed as these solvents in this invention.

Therefore, the parameters for suitable solvents in this invention are (a) compounds that are solvents for the starting carbamate (b) compounds that are stable in the reaction temperature and (c) compounds that are non-reactive with the generated isocyanate.

In view of these criteria or parameters, compounds such as alcohols and acids cannot be used because of their reactivity with the generated isocyanate. Water also must, of course, be excluded.

When operating at atmospheric pressure the boiling point of the solvent or solvent mixture should be at or above the desired operating temperature. Lower boiling solvents or mixtures of solvents can be used by employing superatmospheric pressures; however, since the reaction must be carried out in the liquid phase, the single solvent or solvent mixture cannot have a critical temperature below 175°C (the minimum reaction temperature).

In general, the solvent will be a compound or mixture of compounds selected from the aromatic hydrocarbons having from 1 to 3 rings including the alkyl benzenes having from 1 to 15 carbon atoms in the alkyl group, the halo (particularly chloro) substituted and the mono-nitro substituted derivatives of these aromatics; the aliphatic hydrocarbons having 4 to 32 carbon atoms and the halo (particu-

larly chloro and fluoro) and mono-nitro substituted derivatives of these aliphatics, the cycloaliphatic hydrocarbons, oxygenated compounds having from 4 to 32 carbon atoms and selected from ethers, ketones and esters, and the sulfur analogues of these oxygenated compounds.

More specifically suitable compounds either for the reaction medium or carrier solvent include alkanes or monoalkenes having from 5 to as many as 32 carbon atoms which can be either straight or branched chain, e.g. the pentanes, hexanes, heptanes, octanes, nonanes, decanes and on up to the higher alkanes such as *n* - hexadecane, *n* - octadecane, eicosane and squalane, and the corresponding monoalkenes. Compounds such as the C_4 's, although having critical temperatures below 175°C, can be employed in conjunction with the compounds having critical temperatures above 175°C provided that the mixture has a critical temperature above 175°C. The aromatics such as benzene, toluene, *ortho* - xylene, *meta* - xylene, *para* - xylene, mixtures of two or more of the xylenes, ethylbenzene, cumene, diisopropylbenzenes, dibutylbenzenes, naphthalene, C_1 - C_4 alkyl substituted naphthalenes, substituted benzenes and substituted naphthalenes non-reactive with isocyanates such as the nitro or halogenated compounds for example, the chlorobenzenes, nitrobenzene and chloronaphthalenes diphenyl and substituted diphenyls, diphenyl methane, terphenyls, such as *ortho* - terphenyl, substituted terphenyls, anthracenes and phenanthrenes can be employed with equal utility. Likewise cycloaliphatic hydrocarbons such as cyclopentane, methyl cyclopentane, 1,1 - dimethyl cyclopentane, ethyl cyclopentane, cyclohexane, methyl cyclohexane, ethyl cyclohexane, cycloheptane and others of 5 to 7 carbon atoms.

Ethers (including cyclic ethers) and polyether solvents which do not contain a substituent group which would react with an isocyanate can also be used. Likewise, other oxygen containing compounds such as the ketones, for example methyl ethyl ketone, esters, for example dibutyl phthalate, dihexyl phthalate, dioctyl phthalate and didecyl phthalate are suitable as are the sulfur analogues of these compounds.

In summary compounds meeting the criteria which have been set forth can be employed as the reaction medium solvent or carrier solvent since in order to meet the objectives of the invention, the conversion of the ester of the carbamic acid to give the isocyanate and alcohol must take place in solution from which the isocyanate and alcohol can be recovered without reaction of the isocyanate with the solvent.

The following Examples are provided to illustrate the invention in further detail but these are not to be construed as limiting.

In the runs which follow except where noted differently the ester of the carbamic acid and solvent (when used) were placed in a pot containing a glass covered magnetic stirrer, a thermometer, a nitrogen inlet extending below the liquid level and a 6 inch Vigreux column. The overhead take off tube was connected to a trap maintained at room temperature and then to a set of two Dry-Ice traps to collect the alcohol. The column and overhead tube were not heated during these runs except where noted. In certain runs samples of the pot materials were taken with a syringe inserted through a septum during reaction and were immediately diluted with a weighed amount of dried tetrahydrofuran to insure solubility of the products. In other runs the entire reaction product was analyzed. The samples or entire product were analyzed by gas-liquid phase chromatography for the isocyanate and, for the mono- and/or dicarbamate, by analytical liquid chromatography. In the representative runs which follow, the rate of nitrogen flow is generally about 10 litres per hour or higher. The nitrogen flow rate was merely adjusted to remove the alcohol as formed in the particular laboratory set up employed in these runs and was merely a matter of convenience, whereas in the alternative methods which would be used commercially employing solvents an inert gas would not be required.

EXAMPLE I

A mixture of 10 g ethyl carbanilate (0.0606 mols) and 50 g *n* - hexadecane was heated for 1 hour at 200°C and for 2 additional hours at 220°C in a nitrogen stream at 30 litres per hour. The ethanol carried overhead was collected in a Dry-Ice trap. Analysis showed that 62.4 mol per cent of the ethyl carbanilate had been converted and that the yield of ethanol was 88.7 mol per cent and the yield of phenyl isocyanate was 87.9 mol per cent both based on the ethyl carbanilate converted.

EXAMPLE II (Comparative)

In a similar run with the exception that no solvent was employed, the conversion of ethyl carbanilate was 89.2 mol per cent and the yield of ethanol was 86.2 mol per cent but the yield of phenyl isocyanate was only 18.1 mol per cent. Infra-red and gas-liquid phase chromatographic analysis showed that the major by-product of this latter reaction is the carbodiimide which is undesirable since it is the isocyanate that is the desired useful product. This run confirmed results obtained by Dyer et al described hereinbefore.

A number of runs were carried out to produce toluene diisocyanate; all gave good selectivities. Several are shown in the following Examples. Except where otherwise indicated,

in each case the alcohol was carried overhead and collected in a Dry-Ice trap.

EXAMPLE III

A mixture of 10 g diethyl toluene - 2,4-dicarbamate and 50 g n - hexadecane was heated at 260°C in a stream of nitrogen at 25 litres per hour for 1.5 hours. The reaction mixture was diluted with tetrahydrofuran and analyzed for toluene diisocyanate and the mono- and dicarbamates based on the dicarbamate charged. The yield of toluene diisocyanate was 74 mol per cent and the yield of the monocarbamate was 13 mol per cent, while less than 1 mol per cent of the dicarbamate remained. Since the monocarbamate is an intermediate that can be recycled to produce the toluene diisocyanate this represented a potential yield of 88 mol per cent of the diisocyanate.

EXAMPLE IV

A mixture of 7.2 g of diethyl toluene - 2,4 - dicarbamate and 36 g of *ortho* - terphenyl was heated at 250°C for 2 hours in a nitrogen stream at 25 litres per hour. The product was diluted with tetrahydrofuran and the analysis showed the selectivity to toluene diisocyanate was 63.3 mol per cent, the monocarbamate 27.2 mol per cent and unconverted dicarbamate 3.9 mol per cent. Thus the ultimate yield of the toluene diisocyanate was approximately 95 mol per cent.

EXAMPLE V

A mixture of 10 g of diethyl toluene - 2,4 - dicarbamate was heated with 50 g of n - hexadecane at 250°C for 4 hours in a nitrogen stream, selectivity to toluene diisocyanate was 83.4 mol per cent and 9.4 mol per cent to the monocarbamate. Thus the ultimate yield of toluene diisocyanate was approximately 93 mol per cent.

EXAMPLE VI

A mixture of 10 g of dimethyl toluene - 2,4 - dicarbamate and 50 g of *ortho* - terphenyl was heated at 250°C in a nitrogen stream at 50 litres per hour. The top of the reactor was heated so that substantially all of the toluene diisocyanate was carried overhead, with some of the solvent, as it was formed in the reaction. At the end of 1 hour analysis showed a 73 mol per cent yield of toluene diisocyanate and a 15 mol per cent yield of the monocarbamate.

EXAMPLE VII

A mixture of 10 g of diethyl toluene - 2,6 - dicarbamate and n - hexadecane was heated in a nitrogen stream at 30 litres per hour at a temperature of 250°C. At the end of 15 minutes the toluene - 2,6 - diisocyanate was 58.4 mol per cent together with 34.9 mol per cent of the monocarbamate and 1.8

mol per cent of the starting dicarbamate. At the end of 1 hour the yield of toluene - 2,6 - diisocyanate was 78.1 mol per cent together with 12.3 mol per cent of the monocarbamate. This showed that the monocarbamate had been converted to the diisocyanate so that the ultimate yield of diisocyanate was over 90 mol per cent.

EXAMPLE VIII

In this run a different ester was employed together with a mixed solvent. A mixture of 10 g of di(ethoxyethyl)toluene - 2,4 - dicarbamate in 20 g of tetrahydronaphthalene and 30 g of di - 2 - ethylhexyl phthalate was heated at 241°C for 2 hours in a nitrogen stream at 10 litres per hour. The ethoxyethanol was carried overhead along with some of the tetrahydronaphthalene. Analysis showed an 80 mol per cent conversion to isocyanate groups including a yield of 68.2 mol per cent of the toluene - 2,4 - diisocyanate. This run showed that various esters as well as mixed solvents can be employed in the method of this invention with excellent success.

EXAMPLE IX

In order to show that runs could be carried out at low temperatures a run was carried out at 214°C for 3 hours in which 10 g of di(ethoxyethyl)toluene - 2,4 - dicarbamate was heated with 50 g of tetrahydronaphthalene in a nitrogen stream at 11 litres per hour. There is obtained a 53.9 mol per cent conversion to isocyanate groups including a yield of 22.3 mol per cent of the toluene - 2,4 - diisocyanate. This run was used merely to demonstrate that the reaction could be carried out at low temperatures; however, it will be seen that the conversion is correspondingly slower.

EXAMPLE X

A mixture of 10 g of diethyl toluene - 2,4 - dicarbamate, 15 g of tetrahydronaphthalene and 40 g of *ortho* - terphenyl was heated at 259—261°C in a nitrogen stream at 11.4 litres per hour for 1.5 hours. The yield of toluene - 2,4 - diisocyanate was 66.2 mol per cent along with 20.8 mol per cent of the monocarbamate. This demonstrates that excellent ultimate yields of the diisocyanate can be obtained with a mixed solvent and that one solvent can be utilized as a carrier solvent.

EXAMPLE XI

A mixture of 10 g of diethyl toluene - 2,4 - dicarbamate and 50 g of di - 2 - ethylhexyl phthalate was heated in a cylindrical reactor at 250°C for 1 hour. Nitrogen at 32 litres per hour was passed through a fritted disc at the bottom of the reactor. A yield of toluene - 2,4 - diisocyanate of 57.6 mol

per cent together with 28.6 mol per cent of the monocarbamate and 2.5 mol per cent of unconverted dicarbamate was obtained. This run demonstrated that ester type solvents also can be employed in the process of this invention with excellent results.

EXAMPLE XII (Comparative)

Ten grams of diethyl toluene - 2,4 - dicarbamate was heated in a metal bath at 250°C for 1 hour in a nitrogen stream at 30 litres per hour. Analysis showed that only 13.3 mol per cent of toluene - 2,4 - diisocyanate and 12.1 mol per cent of the monocarbamate were obtained along with 12.4 mol per cent of the dicarbamate. This shows that in the absence of solvent over 62 per cent of the dicarbamate was destroyed without forming useful products while as has been shown hereinbefore the same reaction carried out in a solvent gives a dramatically higher mol per cent of desired product.

EXAMPLE XIII (Comparative)

A run similar to that of Example XII except that it was carried out at 260°C in the absence of a solvent gave a product that polymerized in the reaction flask and could not be removed from the flask. These two runs (Example XII and XIII) show the necessity of carrying out the reaction in a solvent if the high yields of the isocyanate are to be obtained.

EXAMPLE XIV

A mixture of 10 g of diisopropyl toluene - 2,4 - dicarbamate and 50 g of n - hexadecane was heated at 250°C in a nitrogen stream at 25 litres per hour bubbling through the solution. Conversion to toluene - 2,4 - diisocyanate was 45 mol per cent at the end of 1-1/2 hours. This run shows that secondary alcohol esters of the dicarbamic acid are amenable to the process of this invention.

EXAMPLE XV

A mixture of 10.7 g (0.03 moles) 1,6 - hexylene dicarbanilate, having the formula, where Ph=phenyl, of:



and 50 g n - hexadecane was heated at 250°C for two hours in a nitrogen stream at 50 litres per hour. In this Example, the isocyanate was recovered overhead and the alcohol remained in the pot. Analysis of the products taken overhead during the run showed that the yield of phenyl isocyanate produced under these conditions was 57.2 mol per cent. The material remaining in the pot included unreacted carbamates so longer reaction time would have produced additional phenyl isocyanate at a very high ultimate yield.

EXAMPLE XVI

A mixture of 10 grams of diethyl toluene - 2,4 - dicarbamate and 50 grams of technical grade n - octadecane was heated at 250°C in a stream of nitrogen at 30 litres per hour for 1 hour. The yield of toluene diisocyanate was 59.8 mole per cent and the yield of the monocarbamate was 24.4 mole per cent while 1.4 mole per cent of the dicarbamate remained unreacted. Thus the ultimate yield of toluene diisocyanate was approximately 86 mole per cent.

As pointed out hereinbefore, alkyl substituted benzenes having from 1 to 15 carbon atoms in the alkyl side chain can be employed as the solvent. The monoalkyl benzenes having from 9 to 15 carbon atoms in the alkyl side chain are particularly useful and are available as so-called "detergent alkylate" since these compounds when sulfonated and neutralized produce the alkyl benzene sulfonates widely used in both household and industrial detergent formulations. The detergent alkylates are available generally as mixtures of compounds varying only in the number of carbon atoms in the side chain. For example, the commercial material may contain from 10 to 15 carbon atoms in the side chain with over 90 weight per cent of the compounds having from 12 to 14 carbon atoms in the side chain and with the average being 13 carbon atoms in the side chain. Other commercial materials have other distributions of alkyl side chains. The alkyl side chains may be either straight chain or branched chain, but most commercial detergent alkylate available in recent years contains only straight chain compounds since these give biodegradable detergents whereas the branched chain compounds give detergents resistant to biodegradation and hence are no longer in general use.

The following Examples are provided to show the use of commercial detergent alkylates as solvents. As in most of the previous Examples, in each case (except where otherwise indicated), the alcohol was carried overhead and collected in a Dry-Ice Trap.

EXAMPLE XVII

A mixture of 10 g diethyl toluene - 2,4 - dicarbamate and 50 g of a commercial detergent alkylate, having about 10 to 12 carbon atoms in the alkyl side chain, with small amounts of higher and lower compounds and with an average side chain of about 11.3 carbon atoms attached to the benzene ring, was heated at 250°C in a stream of nitrogen at 30 litres per hour for 1 hour. The reaction mixture was diluted with tetrahydrofuran and analyzed for toluene diisocyanate and the mono- and dicarbamate based on the dicarbamate charged. The yield of toluene diisocyanate was 52 mole per cent and the yield of the monocarbamate was 41.6 mole per

cent, while 4 mole per cent of the dicarbamate remained. Thus, the ultimate yield of the toluene diisocyanate was over 97 mole per cent.

EXAMPLE XVIII

A mixture of 10 g diethyl toluene - 2,4 - dicarbamate and 50 g of a commercial detergent alkylate having from 10 to 15 carbon atoms in the side chain, with over 90 weight per cent having from 12 to 14 carbon atoms and with an average side chain of 13 carbon atoms attached to the benzene ring, was heated at 250° in a stream of nitrogen at 30 litres per hour for 1 hour. The yield of toluene diisocyanate was 59.1 mole per cent and the yield of monocarbamate was 25.7 mole per cent while 1.4 mole per cent of the dicarbamate remained. Thus, the ultimate yield of toluene diisocyanate was over 86 mole per cent.

In order to demonstrate continuous operation, the following runs were made.

EXAMPLE XIX

The detergent alkylate of Example XVII in the amount of 100 ml was placed in a 300 ml round-bottom flask fitted with two feed inlet tubes, a nitrogen inlet tube, a 12" Vigreux column, a thermometer and a product dip tube. A solution containing 0.12 g diethyl toluene - 2,4 - dicarbamate per ml of tetrahydrofuran solution was pumped in at the rate of about 32 ml per hour; the detergent alkylate was pumped in at approximately 8 to 10 ml per hour to maintain a level sufficient to give an average residence time of about 15 hours. A stream of nitrogen was passed in at a rate of 30 litres per hour. The pot temperature was maintained at 250°C and the column was wrapped to give a temperature of 130°C at the top of the column. Under steady state conditions, the yield of toluene diisocyanate recovered overhead was 81 mole per cent along with 3 mole per cent of monocarbamate. In addition, 2 mole per cent toluene diisocyanate, 5 mole per cent monocarbamate and 2 mole per cent dicarbamate were present in the product drawn from the pot to give a total yield of 93 mole per cent.

EXAMPLE XX

In the same unit as described in Example XIX, the detergent alkylate was replaced with n - hexadecane. Other conditions were similar except for a top column temperature of 180°C. Under steady state conditions with an average residence time of about 20 hours, the yield of toluene diisocyanate recovered overhead was 84 mole per cent along with 9 mole per cent monocarbamate. In addition, 1 mole per cent toluene diisocyanate, 2 mole per cent monocarbamate and 1 mole per cent dicarbamate were present in the product

drawn from the pot to give a total yield of 97 mole per cent.

Examples XVII and XVIII show that alkyl benzenes having up to 15 carbon atoms in the alkyl side chain, i.e., the detergent alkylates can be employed as solvents in the method of this invention. Examples XIX and XX demonstrate continuous operation and show that exceedingly high yields are obtainable thereby.

All the foregoing Examples demonstrate the utility of the invention for generating isocyanates corresponding to various esters of various carbamic acids by utilizing the solvent method of this invention with atmospheric pressure pyrolysis. The results show that high yields of isocyanates are obtainable even from esters of dicarbamic acids which heretofore, in general, gave little if any yield of the diisocyanate by pyrolysis methods. Of particular interest the results show that in the conversion of the dicarbamates there is formed the monocarbamate intermediate which on continued conversion (or recycle) is converted to the diisocyanate.

WHAT WE CLAIM IS:—

1. A method for the production of isocyanates from esters of carbamic acids having the formula



or



wherein each R is a substituted or unsubstituted mono-, di or trivalent organic radical selected from saturated and monoolefinic unsaturated straight and branched chain aliphatic and cycloaliphatic radicals containing not more than 32 carbon atoms, alkoxyalkyl radicals having not more than 32 carbon atoms, and aryl radicals aralkyl radicals and alkaryl radicals containing 1 to 5 rings; each R' is a substituted or unsubstituted mono-, di or trivalent radical selected from saturated and monoolefinic unsaturated straight and branched chain aliphatic and cycloaliphatic radicals containing not more than 32 carbon atoms, alkoxyalkyl radicals having not more than 32 carbon atoms, and aryl radicals aralkyl radicals, and alkaryl radicals containing 1 to 3 rings; and x is 1, 2 or 3, each R or R' being the same or different, respectively, where x is 2 or 3, said method comprising thermally decomposing said ester at a temperature in the range of from 175°C to 350°C while said ester is dissolved in an inert solvent to produce the isocyanate and alcohol, and separately recovering said isocyanate and alcohol; said solvent being characterized as a compound or mixture of compounds which is (a) a solvent for said

cent, while 4 mole per cent of the dicarbamate remained. Thus, the ultimate yield of the toluene diisocyanate was over 97 mole per cent.

EXAMPLE XVIII

A mixture of 10 g diethyl toluene - 2,4 - dicarbamate and 50 g of a commercial detergent alkylate having from 10 to 15 carbon atoms in the side chain, with over 90 weight per cent having from 12 to 14 carbon atoms and with an average side chain of 13 carbon atoms attached to the benzene ring, was heated at 250° in a stream of nitrogen at 30 litres per hour for 1 hour. The yield of toluene diisocyanate was 59.1 mole per cent and the yield of monocarbamate was 25.7 mole per cent while 1.4 mole per cent of the dicarbamate remained. Thus, the ultimate yield of toluene diisocyanate was over 86 mole per cent.

In order to demonstrate continuous operation, the following runs were made.

EXAMPLE XIX

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EXAMPLE XX

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drawn from the pot to give a total yield of 97 mole per cent.

Examples XVII and XVIII show that alkyl benzenes having up to 15 carbon atoms in the alkyl side chain, i.e., the detergent alkylates can be employed as solvents in the method of this invention. Examples XIX and XX demonstrate continuous operation and show that exceedingly high yields are obtainable thereby.

All the foregoing Examples demonstrate the utility of the invention for generating isocyanates corresponding to various esters of various carbamic acids by utilizing the solvent method of this invention with atmospheric pressure pyrolysis. The results show that high yields of isocyanates are obtainable even from esters of dicarbamic acids which heretofore, in general, gave little if any yield of the diisocyanate by pyrolysis methods. Of particular interest the results show that in the conversion of the dicarbamates there is formed the monocarbamate intermediate which on continued conversion (or recycle) is converted to the diisocyanate.

WHAT WE CLAIM IS:—

1. A method for the production of isocyanates from esters of carbamic acids having the formula



or



wherein each R is a substituted or unsubstituted mono-, di or trivalent organic radical selected from saturated and monoolefinic unsaturated straight and branched chain aliphatic and cycloaliphatic radicals containing not more than 32 carbon atoms, alkoxyalkyl radicals having not more than 32 carbon atoms, and aryl radicals aralkyl radicals and alkaryl radicals containing 1 to 5 rings; each R' is a substituted or unsubstituted mono-, di or trivalent radical selected from saturated and monoolefinic unsaturated straight and branched chain aliphatic and cycloaliphatic radicals containing not more than 32 carbon atoms, alkoxyalkyl radicals having not more than 32 carbon atoms, and aryl radicals aralkyl radicals, and alkaryl radicals containing 1 to 3 rings; and x is 1, 2 or 3, each R or R' being the same or different, respectively, where x is 2 or 3, said method comprising thermally decomposing said ester at a temperature in the range of from 175°C to 350°C while said ester is dissolved in an inert solvent to produce the isocyanate and alcohol, and separately recovering said isocyanate and alcohol; said solvent being characterized as a compound or mixture of compounds which is (a) a solvent for said



- ester, (b) liquid and stable at said decomposition temperature and (c) non-reactive with said isocyanate produced in said thermal decomposition reaction, and selected from aliphatic hydrocarbons having from 4 to 32 carbon atoms, halo- and mono-nitro substituted derivatives of said aliphatic hydrocarbons, cycloaliphatic hydrocarbons, aromatic hydrocarbons having from 1 to 3 rings, alkyl benzenes having from 1 to 15 carbon atoms in the alkyl group, halo- and mono-nitro substituted derivatives of said aromatic hydrocarbons and alkylbenzenes, oxygenated compounds containing from 4 to 32 carbon atoms and selected from ethers, ketones and esters of organic carboxylic acids, and sulfur analogues of said oxygenated compounds.
2. A method according to Claim 1 wherein the decomposition temperature is in the range of from 200°C to 300°C.
3. A method according to Claim 1 or Claim 2 wherein R is selected from mono-, di- and trivalent unsubstituted organic aliphatic radicals containing up to 18 carbon atoms; halo or mono-nitro substituted mono-, di- and trivalent organic aliphatic radicals containing up to 18 carbon atoms; mono-, di- and trivalent cycloaliphatic radicals containing from 5 to 7 carbon atoms; mono-unsaturated cycloaliphatic radicals having from 5 to 7 carbon atoms and substituted cycloaliphatic radicals wherein the substituent is an alkyl radical having 1 to 4 carbon atoms, a nitro radical or a chloro radical.
4. A method according to Claim 1 or Claim 2 wherein R is an alkoxyalkyl radical having up to 18 carbon atoms.
5. A method according to Claim 1 or Claim 2 wherein R is selected from mono-, di- and trivalent unsubstituted aryl radicals having from 1 to 5 rings, aryl radicals substituted with 1 or more alkyl groups having from 1 to 4 nitro groups or halo groups, and aralkyl radicals wherein the alkyl portion contains from 1 to 4 carbon atoms and the aryl contains from 1 to 3 rings.
6. The method according to any one of Claims 1 to 5 wherein R' is selected from mono-, di- and trivalent unsubstituted organic aliphatic radicals containing up to 18 carbon atoms, halo or mono-nitro substituted mono-, di- or trivalent organic aliphatic radicals containing up to 18 carbon atoms and alkoxyalkyl radicals containing up to 18 carbon atoms.
7. A method according to any one of Claims 1 to 6 in which the isocyanate is a toluene diisocyanate.
8. A method according to Claim 7 wherein said toluene diisocyanate is toluene - 2,4 - diisocyanate.
9. A method according to any one of Claims 1 to 8 wherein said solvent is *ortho*-terphenyl.
10. A method according to any of Claims 1 to 8 wherein said solvent is tetrahydronaphthalene.
11. A method according to any one of Claims 1 to 8 wherein said solvent is *n* - hexadecane.
12. A method according to any one of Claims 1 to 8 wherein said solvent is *n* - octadecane.
13. A method according to any one of Claims 1 to 8 wherein said solvent is di - 2 - ethylhexyl phthalate.
14. A method according to any one of Claims 1 to 8 wherein said solvent is a mixture of alkyl benzenes having from 9 to 15 carbon atoms in the alkyl group.
15. A method according to Claim 14 wherein said mixture of alkyl benzenes has from 10 to 12 carbon atoms in the alkyl group with an average of about 11 carbon atoms.
16. A method according to Claim 14 wherein said mixture of alkyl benzenes has from 10 to 15 carbon atoms in the alkyl group with an average of about 13 carbon atoms.
17. A method according to Claim 1 for the production of isocyanates from esters of carbamic acids, substantially as hereinbefore described with particular reference to the Examples.
18. Any method which is substantially a method described herein as an embodiment of the method claimed in Claim 1.
19. An isocyanate obtained by the method claimed in any one of Claims 1 to 18.

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