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[54] **GEM CYCLODIALKYLATION OF AMINES AND AMIDES**

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[58] **Field of Search** 546/192; 548/322, 540, 548/562, 563, 564, 570, 577, 579

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[57] **ABSTRACT**

Amines and amides are N,N-cyclodialkylated by reaction with an unstrained cyclic ether in the presence of a B-subgroup metal oxide alkylation catalyst, preferably a Group IV-B metal oxide such as titanium dioxide.

21 Claims, No Drawings

GEM CYCLODIALKYLATION OF AMINES AND AMIDES

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

REFERENCE TO RELATED APPLICATION

[This is] *This is a reissue of application Ser. No. 685,854, filed Dec. 24, 1984, now U.S. Pat. No. 4,626,592, which is* a continuation-in-part of prior copending application Ser. No. 618,005, filed June 6, 1984[.], *now U.S. Pat. No. 4,721,810.*

FIELD

This invention relates to an improved catalytic process for the alkylation of aromatic amines and other organic derivatives of ammonia. More particularly, this invention relates to a catalytic process for the N,N-cyclodialkylation of amino and/or amido groups.

BACKGROUND

Numerous methods, processes, and catalysts have been described for alkylating aromatic amines to provide valuable and useful chemical products. However, the previous suggestions have various defects including lack of selectivity of the desired product, poor conversion of the aromatic amine, and excessive deterioration of the alkylating agent which then cannot be recovered for recycle or other use.

My prior copending application Ser. No. 618,005, file June 6, 1984 describes, inter alia, a process which comprises the step of reacting (a) an aromatic amine having at least one replaceable hydrogen atom on an amine group or on an aromatic ring carrying an amino group or both, with (b) an ether in the presence of a B-subgroup metal oxide alkylation catalyst so that alkylation of the aromatic amine occurs. In that application it is disclosed that such cyclic ethers as tetrahydrofuran, tetrahydropyran and their suitably substituted congeners react with primary aromatic amines such as aniline and nuclear alkylanilines (e.g., toluidines, xylidines, o-, m-, p-ethylaniliane, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-and 3,5-diethylanilines, etc.) whereby gem-dialkylation of the nitrogen atom occurs and N-arylated cycle amines are formed. This reaction has now been found to apply to various additional reaction combination beyond primary aromatic amines and cyclic ethers such as tetrahydrofuran, tetrahydropyran and their suitably substituted congeners. The expanded horizons of the process of this invention will become apparent from the ensuing description and appended claims.

THE INVENTION

In accordance with one embodiment of this invention an efficacious process for converting an N,N-dialkylatable amino or amido group into an N,N-cyclodialkylated amino or amido group is provided This process comprises reacting a compound containing at least one N,N-dialkylatable amino or amido group with an unstrained cyclic ether co-reactive therewith in the presence of a viable B-subgroup metal oxide alkylation catalyst so that at least one such N,N-dialkylatable amino or amido group is transformed into an N,N-cyclodialkylated amino or amido group, respectively.

In this embodiment of the invention use is made of aliphatic, cycloaliphatic, aromatic, and heterocyclic compounds that contain at least one N,N-dialkylatable amino or amido group. The characteristics of the N,N-dialkylatable amino groups are the following:

(1) The amino groups are not so sterically hindered as to prevent the derived N,N-cyclodialkylation from occurring.

(2) The amino groups are substituted by at least one, and preferably by two, hydrogen atoms. When substituted by only one hydrogen atom, a second bond of the amino group is satisfied by a group, such as methyl, that can be displaced in the course of the N,N-cyclodialkylation reaction. In other words, the amino group has the formula

$$-\mathrm{NHR}$$

wherein R is hydrogen or a displaceable substituent such as an alkyl group or the like.

(3) The amino groups are bonded to organic groups or moieties that do not prevent the N,N-cyclodialkylation reaction from occurring.

The characteristics of the N,N-cyclodialkylatable amido groups are as follows:

(1) They have the formula

$$-\mathrm{CONH}_2$$

(2) They are bonded to organic groups or moieties that do not prevent the N,N-cyclodialkylation reaction from occurring.

In short, the practice of this embodiment of the invention utilizes only amines and amides that undergo the desired cyclodialkylation reaction under the reaction conditions employed.

In other embodiments of this invention, the process comprises the step of reacting (a) an aromatic amine having at least one replaceable hydrogen atom on an amine group or on an aromatic ring carrying an amino group or both, with (b) an ether in the presence of a B-subgroup metal oxide alkylation catalyst so that alkylation of the aromatic amine occurs. When effecting nuclear alkylation (i.e., alkylation on the ring), best results are achieved when the aromatic amine has at least one primary amino group on an aromatic ring and has a replaceable hydrogen on the ring in at least an ortho or para position relative to such amino group.

A preferred embodiment of this invention involves using as the catalyst in the foregoing reactions a metal oxide alkylation catalyst consisting essentially of at least about 70 mole % (i.e., about 70 to 100%) of a Group IV-B metal oxide, most preferably a titanium oxide (especially TiO_2) and up to about 30 mole % (i.e., 0 to about 30%) of (i) a Group VI-B metal oxide, most preferably a molybdenum oxide (especially MoO_3) or (ii) a Group VIII metal oxide, most preferably an iron oxide (especially Fe_2O_3), or (iii) a mixture of (i) and (ii).

A particular advantage of my process is that under most reaction conditions ether alkylating agents such as diethyl ether not consumed in the alkylation reaction pass through the reaction zone undecomposed and thus can be readily recovered for recycle or other use. In addition, my process involves use of catalysts which are easily prepared, and which in many cases have superior catalytic activity and long useful lives.

Another feature of this invention is that when alkylating aromatic amines, the nature of the alkylation product can be varied considerably depending upon the nature of the B-subgroup metal oxide alkylation catalyst used. For example, to achieve substantial alkylation on the primary amino group (—NH_2) on an aromatic ring which itself contains one or more replaceable hydrogen atoms, it is desirable to employ a Group IV-B metal oxide alkylation catalyst such as TiO_2, ZrO_2, or the like. In fact, with a zirconia catalyst, reaction between aniline and diethylethyer at 325° C. resulted in 95% conversion and 94.5% yield of N-ethylated products. To increase the proportion of ring alkylation relative to nitrogen alkylation, use may be made as the alkylation catalyst of a Group IV-B metal oxide combined with a minor proportion (usually 20% by weight or less) of a Group VI-B metal oxide such as MoO_3, WO_3 or the like. Use of a minor proportion of a Group VIII metal oxide such as Fe_2O_3 in combination with a Group IV-B metal oxide alkylation catalyst also tends to increase the ratio of ring alkylation to nitrogen alkylation. When a Group II-B metal oxide alkylation catalyst such as ZnO is employed by itself as the catalyst, alkylation tends to be focused on the nitrogen atom.

The reaction conditions used also tend to affect the course of the aromatic amine alkylation reaction. In general, when an opportunity exists for both ortho and para alkylation to occur, the use of higher reaction temperatures tends to promote an increase in orthoalkylation especially when using TiO_2-based alkylation catalysts. For example, reaction between aniline and diethylether using a 90% TiO_2-10% Fe_2O_3 catalyst gave an o-ethylaniline/p-ethylaniline ratio of 4.3 at 350° C., whereas at 375° C. the ratio was 5.7. Likewise, the addition of water to the feed stream tends to increase the ortho/para ratio of the ring alkylated products.

According to the present invention, ethers have been found to be very effective for alkylating various alkylatable aromatic amines in the presence of a B-subgroup metal oxide alkylation catalyst. While product selectivity is usually at least as good as the processes known to the prior art, this invention also offers the additional advantage of making possible conversion rate somewhat higher than with processes disclosed in the prior art. Furthermore, in the process of this invention it is possible to achieve almost complete recovery of the ether which passes through the reaction zone without participating in the alkylation reaction. This of course, enables the ether to be reused in the present process or to be used for other purposes.

The present invention is carried out at an elevated temperature conventional for catalytic alkylation processes. The temperature of reaction for the present process is usually about 200° C. or higher, preferably 300° C. or higher, although in some cases, for example in liquid phase reactions where long reaction periods can be used, temperatures below 200° C. are satisfactory. More preferably, the alkylation process of the present invention is carried out at an elevated temperature in the range of about 350°-450° C. While higher temperatures may be used, the temperature used should take into consideration the thermal decomposition temperatures of the reactants and products as well as the effect of temperature on the activity of the particular heterogeneous catalyst system being employed. In general, the most preferred temperatures for the alkylation process fall in the range of from about 350° to about 425° C. For the N,N-cyclodialkylation process temperatures in the range of about 200° to about 350° C. are most preferred.

When the aromatic amine alkylation process of the present invention is carried out as further described below, the conversion of aromatic amines such as aniline, toluidine, xylidine, and more complex aromatic amines is usually in the range of from less than 5 to as much as 30% or more. The 30% or more figure is considered very satisfactory for most catalytic alkylation processes. In view of the recoverability of the alkylating agent of the present invention, conversions in this range are especially advantageous since the process can be made much more economical with recovery of such a reactant. The process of the present invention is suitably carried out at atmospheric pressure but may be carried out at superatmospheric or subatmospheric pressures.

Numerous aromatic amines are usable according to the process of this invention. Typical aromatic amines usable as starting materials in my process include the single ring compounds such as aniline, o-toluidine, m-toluidine, p-toluidine, o-ethylaniline, m-ethylaniline, p-ethylaniline, o-isopropylaniline, m-isopropylaniline, p-isopropylaniline, 2,3-xylidine, 2,4-xylidine, 2,5-xylidine, 2,6-xylidine, 3,4-xylidine, 3,5-xylidine, 2,3-diethylaniline, 2,4-diethylaniline, 2,5-diethylaniline, 2,6-diethylaniline, 3,4-diethylaniline, 3,5-diethylaniline, 2,3-diisopropylaniline, 2,4-diisopropylaniline, 3,5-diisopropylaniline, and the like. Also usable according to the process of the present invention are the N-alkylated aromatic amines such as N-methylaniline, N-ethylaniline, N-isopropylaniline, N,N-dimethylaniline, N,N-diethylaniline, N,N-diisopropylaniline, N-methyl-o-toluidine, N-methyl-2,3-xylidine, N-methyl-2,4-xylidine, N-methyl-2,5-xylidine, N-methyl-3,5-xylidine, N,N-dimethyl-o-toluidine, N,N-dimethyl-m-toluidine, N,N-dimethyl-p-toluidine, N,N-dimethyl-2,3-xylidine, N,N-dimethyl-2,4-xylidine, N,N-dimethyl-2,5-xylidine, N,N-dimethyl-3,5-xylidine, N-ethyl-o-toluidine, N-ethyl-m-ethylaniline, N-ethyl-p-ethylaniline, N-ethyl-2,3-diethylaniline, N-ethyl-2,4-diethylaniline, N-ethyl-2,5-diethylaniline, N-ethyl-3,5-diethylaniline, N,N-diethyl-o-ethylaniline, N-ethyl-3,5-diethylaniline, N,N-diethyl-o-ethylaniline, N,N-diethyl-m-ethylaniline, N,N-diethyl-p-ethylaniline, and the like. Also usable in the process of this invention are multiple ring compounds such as diphenylamine, 4-aminobiphenyl, 1-naphthylamine, 2-naphthylamine, 1-anthrylamine, 1-phenanthrylamine, 1,4-diaminonaphthalene, 1,5-diaminonaphthalene, and the like. Similarly the aromatic diamines, triamines, and other polyamines are usable. Examples of such compounds include 2,4-toluenediamine, 2,5-toluenediamine, 1,3-diaminobenzene, 4,4′-methylenebisaniline, 1,3,5-triaminobenzene, and the like.

Suitably substituted aromatic amines may also be used, such as o-anisidine (2-aminoanisole), m-anisidine, p-anisidine, o-chloroaniline, m-chloroaniline, p-chloroaniline, anthranilonitrile (o-aminobenzonitrile or o-cyanoaniline), and the like.

Of the above described aromatic amines, the single ring aromatic amines are preferred. Aniline and ring alkylated anilines are the more preferred of the single ring aromatic amines. Most preferred are aniline, one or a mixture of two or more toluidine isomers or one or a mixture of two or more xylidine isomers.

Various ethers are usable in the present aromatic amine alkylation process. These include acyclic ethers, i.e., ethers in which the ether oxygen is not in a ring system, and unstrained cyclic ethers. Useful acyclic ethers include alkyl ethers, (either straight or branched chain), cycloalkyl ethers, aromatic ethers, and ethers which are mixtures of these types. A preferred class of ethers are the dialkyl ethers where the alkyl groups are either the same or different and at least one of them is a primary alkyl group. These include dimethyl ether, dibutyl ether, ethyl propyl ether, ethyl octyl ether, diiobutyl ether, ethyl methyl ether, diisopropyl ether, heptyl methyl ether, methyl tert-butyl ether, and the like. More preferred from the standpoint of reaction selectivity are the dialkyl ethers where the alkyl groups are the same such as dimethyl ether, diisobutyl ether, di-n-propyl ether, di-n-butyl ether, diisobutyl ether, di-n-pentyl ether, and the like. Especially preferred are the di-lower alkyl ethers (i.e., each alkyl group has up to about six carbon atoms), especially those in which the alkyl groups are identical and are primary alkyl groups.

Various unsaturated acyclic ethers are also usable in the aromatic amine alkylation process of the present invention. These include divinyl ether, diallyl ether, dicrotyl ether, and the like.

Various acylic aromatic ethers (e.g., aryl and aralkyl ethers) are also usable in the aromatic amine alkylation embodiments of the present invention. These include dibenzyl ether, diphenyl ether, benzyl phenyl ether, and other such ethers. Also usable are the mixed alkyl and aromatic ethers such as anisole, ethyl phenyl ether, ethyl p-tolyl ether, hexyl phenyl ether, methyl benzyl ether, 2,6-dimethoxypyridine, 2,4-dimethoxypyrimidine, and the like.

Also usable for alkylating aromatic amines are the acyclic cycloalkyl ethers such as dicyclopentyl ether, dicyclohexyl ether, and the like. Also mixed cycloalkyl ethers, such as cyclopentyl cyclohexyl ether, are usable for this purpose. Furthermore, mixed ethers having a cycloalkyl substituent and another substituent are also usable for aromatic amine alkylation according to the present invention. These include, for example, methyl cyclopentyl ether, benzyl cyclohexyl ether, ethyl cyclopropylcarbinyl ether, and the like.

Also usable for aromatic amine alkylation according to the present invention are the glycol ethers such as the ethylene glycol ethers and propylene glycol ethers including 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dimethoxypropane, 1,3-diethoxypropane, and the like. Cyclic polyethers such as 1,3-dioxolane, 1,4-dioxane, 1,3,5-trioxane and the like can also be used in the alkylation process.

Generally speaking, most ethers having the linkage C—O—C are usable for alkylating aromatic amines according to the present invention although in some cases unreactive types of ethers may be encountered. Thus, I utilize in the present process only ethers that are co-reactive with the alkylatable aromatic amines so that alkylation occurs. In this connection, the term "alkylation" is used herein in a generic sense to indicate that an organic group of the ether reactant, whether alkyl, aryl or etc., is introduced into the molecular of the aromatic amine reactant. Likewise the term "cyclodialkylation" is used herein a generic sense to indicate that a cyclic group is formed on the nitrogen atom of the gem (i.e., N,N—)dialkylatable amino or amido group(s), which cyclic group may be saturated or unsaturated and may be composed solely of the nitrogen atom and carbon atoms or may contain one or more additional hetero atoms.

When conducting the N,N-cyclodialkylation reaction of this invention the co-reactant is an unstrained cyclic ether that undergoes the N,N-cyclodialkylation reaction under the reaction conditions being used and with the amine or amide being used.

The characteristics of such ethers are as follows:

(1) They contain at least one oxygen atom in an at least five-membered ring system that is susceptible to ring opening under the reaction conditions employed.

(2) The ring system is free of ring components and ring substituents that prevent the N,N-cyclodialkylation reaction from occurring.

Among the cyclic ethers suitable for the practice of this invention are those which contain only carbon and an oxygen atom in an unstrained ring (i.e., the ring contains at least four carbon atoms and an oxygen atom bonded to two separate carbon atoms of the ring). Examples of such cyclic ethers include tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, tetrahydro-2-furancarbinol, 2-ethoxymethyl tetrahydrofuran, 2-butoxymethyl tetrahydrofuran, tetrahydrofuroic acid, methyl tetrahydrofuroate, tetrahydropyran, 2-methyltetrahydropyran, furan, dihydrofuran, pyran, dihydropyran, and the like. In the case of such cyclic ethers as tetrahydrofuran, tetrahydropyran and their suitably substituted congeners, reaction with primary aromatic amines such as aniline and nuclear alkylanilines (e.g., toluidines, xylides, o-, m-, p-ethylaniline, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-diethylanilines, etc.) results in gem-dialkylation of the nitrogen atom with high conversions of the aromatic amines and very high product yields. For example, reaction between tetrahydrofuran and aniline at 250° C. using a TiO_2 catalyst (LHSV of 0.2 per hour) gave a 98% conversion of aniline with a 97% yield of 1-phenylpyrrolidine. Similary, tetrahydropyran and aniline when reacted at 300° C. over a TiO_2 catalyst (LHSV of 0.2 per hour) resulted in a 74% aniline conversion with a 98% yield of 1-phenylpiperidine.

Various types of cyclic ethers may be used in the N,N-cyclodialkylation process of this invention. For example, use may be made of such diverse compounds as furan; the various dihydrofuran and dihydropyran isomers; alkyl-substituted furans, dihydrofurans, tetrahydrofurans, dihydropyrans and tetrahydropyrans, such as 2,5-dimethyltetrahydrofuran; gamma-butyrolactone; furfuryl alcohol; hydroxy and alkoxy-substituted furans, dihydrofurans, tetrahydrofurans, dihydropyrans and tetrahydropyrans, such as 2-methoxytetrahydrofuran and 3-hydroxytetrahydrofuran; furfurylamine; 2-furaldehyde; oxepane; and the like. Moreover, unstrained cyclic ethers having nitrogen in the ring such as 2-oxazolidone (which may also be considered a heterocyclic amine) can be used in the process.

In the N,N-cyclodialkylation process primary aromatic amines, such as those exemplified above, may be used. In addition, secondary aromatic amines may be used provided one of the substituents on the nitrogen atom is displaceable under the reaction conditions being used. Examples of such compounds include the N-alkylanilines, such as N-methylaniline, N-ethylaniline, N-methyl-p-chloroaniline, and various other similar compounds.

Moreover the N,N-cyclodialkylation process of this invention can be applied to aliphatic amines, such as methylamine, ethylamine, propylamine, butylamine, octylamine, dodecylamine, tetradecylamine, allylamine, benzylamine, 1-adamantanemethylamine (i.e., 1-aminomethyladamantane), ethanol amine, 2-chloroethylamine, etc.; cycloaliphatic amines such as cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, cyclooctylamine, cyclododecylamine, 1-adamantanamine, 1-aminoindan, etc.; and heterocylic amines, such as 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, adenine, 2-amino-5-picoline, 2-amino-6-picoline, aminopyrazine, 2-aminopyrimidine, 9-amino-1,2,3,4-tetrahydroacridine, and the like.

Amides that can be used in the N,N-cyclodialkylation process of this invention are exemplified by formamide, acetamide, propionamide, and the like.

The present invention is capable of being carried out in either a batch or continuous operation mode according to the available equipment and intentions of the operator. In addition, the various processes may be carried out either in the vapor phase or in the liquid phase, depending of course upon the reactants and temperature and pressure conditions in use. When conducted as a liquid phase process the reactants may be subjected to reaction either in bulk or in a suitable inert reaction solvent or diluent such as an inert hydrocarbon that exists in the liquid state under the reaction conditions being employed.

According to the invention, various catalysts may be used so long as the catalyst consists essentially of a B-subgroup metal oxide of suitable activity in the alkylation reaction under consideration. As is well known, Group I-B is composed of copper, silver and gold whereas Group II-B is composed of zinc, cadmium and mercury. Scandium, yttrium and the lathanide and actinide series make up Group III-B. Group IV-B consists of titanium, zirconium and hafnium, Group V-B consists of vanadium, niobium and tantalum, Group VI-B consists of chromium, molybdenum and tungsten, and Group VII-B consists of manganese, technetium and rhenium. Various oxides of such metals that are viable catalysts for the alkylation are within the ambit of this invention. Aromatic amine alkylation catalysts composed of mixtures of two or more different oxides of the same B-subgroup metal (e.g., TiO_2 and Ti_2O_3, etc.), composed of oxides of two or more different metals of the same B-subgroup (e.g., TiO_2 and ZrO_2; TiO_2, ZrO_2 and HfO_2, etc.), and composed of oxides of two or more metals of different B-subgroups (e.g., TiO_2 and MoO_3, TiO_2 and WO_3, TiO_2 and ZnO, etc.) may also be used. Various other oxides usable as additional components of the catalysts of the present invention such as one or more oxides of aluminum, antimony, barium, beryllium, bismuth, calcium, cobalt, gallium, germanium, iron, lead, magnesium, nickel, osmium, potassium, silicon, sodium, tin, and the like may be prepared by any of the known means and combined with the B-subgroup metal oxide catalysts according to the invention. Catalysts composed of one or more B-subgroup metal oxides in combination with one or more non-B-subgroup metal oxides should predominate (on a molar basis) in the B-subgroup metal oxide(s). In fact, such mixed oxide catalysts preferably contain at least 70 mole % of one or more B-subgroup metal oxides and no more than about 30 mole % of one or more non-B-subgroup metal oxides.

As noted above, it is important when practicing this invention to use an active alkylation catalyst for the process. In this connection, the thermal history of the catalyst appears to be of importance to its activity. For example, a highly active titania catalyst for the process of this invention after having been heated to 450° C. was found to have lost a substantial amount of its catalytic activity for the process. And after heating the catalyst to 650° C., this catalyst was found to be totally ineffective for use in my process. Thus any given commercially available B-subgroup metal oxide catalyst may or may not be active in the process of this invention depending upon whether or not it was calcined and if so, whether the calcining temperature was high enough to destroy its catalytic activity for use in the process of this invention. Thus in selecting commercially available B-subgroup metal oxides for use in my process, one should attempt to secure materials that have not been calcined at excessively high temperatures that render them unsuitable in the present process. In cases where the manufacturers decline to supply such thermal history information, one should secure and test in the present process a variety of samples of candidate B-subgroup metal oxide catalysts and select one or more having the best or optimum activity for the particular aromatic amine alkylation under consideration. As an example, samples of two different TiO_2 catalysts were obtained from the same commercial manufacturer. X-ray diffraction analysis showed that both were in the anatose phase and indicated that they were identical materials. One of these was found to be a highly active catalyst for use in my process. The other was totally inactive.

Methods for the manufacture of oxides of B-subgroup metals are known and reported in the literature. When utilizing such procedures care should be taken to avoid heating the oxide catalyst to a temperature which destroys or substantially diminishes its catalytic activity in my alkylation process. The catalyst may be supported on or impregnated onto a suitable inert carrier although this is ordinarily unnecessary.

Although the process can be carried out in the liquid phase, it is preferable to conduct the process in the vapor phase using a fixed-bed or a moving or fluidized bed of the catalyst.

The present invention will be still further understood by a review of the following illustrative examples of the best mode of the invention of which I am now aware, in which all of the percentages are expressed on a weight basis unless otherwise specified.

In the ensuing examples use was made of a tubular reactor positioned within an Ohio Thermal wire wound tubular furnace, model T11C-0432. The muffle tube of the furnace was 1½ inches inside diameter and 12 inches long, constructed of fused alumina. A ¼ inch inside diameter thermocouple well was provided adjacent to the heating element. The thermocouple was used to control the series 4DA controller which has a range of 200°-1100° C. The reactor itself was a 19 inch long, 1 inch inside diameter stainless steel tube fitted with an internal thermocouple well. The reactor tube was fitted for supply of helium gas from one line and a second line connected to a Milton Roy pump. The second line fed reactants from a reservoir attached thereto. A water condenser below the reactor tube and an ice bath were used to collect liquid in glassware in the ice bath. The vapors transmitted from the glassware in the ice bath were directed to a dry ice bath and the outlet thereof was connected directly to a gas chromatography unit and then to a wet test meter.

The following procedure was used for all of the runs given in the tables below. The reactor tube was filled with 5 millimeter glass beads to define the catalyst bed location. A weighed amount of catalyst was then suppled to the catalyst bed area and additional 5 millimeter beads were used to fill the tube to the top of the furnace.

All equipment was properly purged and flushed according to good standard laboratory practice. The desired feed for the run was added to the reservoir and the pump and inlet tube as necessary. The ice water bath and dry ice bath were attached, and the helium flush was started at the rate of 20–30 cc per minute during furnace warmup and stabilization. To start a run, the helium was turned off, and the feed pump was turned on at the desired feed rate. The thermocouple temperatures wee recorded along with the feed level and the wet test meter readings. The sampling times were also noted. The product gases were directed to the sample loop of the GC sampling valve and injected onto a 10'×⅛" Poropak TM R column. The traps were removed and immediately replaced with a second set. The liquid samples were combined and weighed. To terminate the run, the feed pumps were turned off and drained for about five minutes before removing the residue therein. Thereafter, the helium flush was again turned on at about 20–30 cc per minute and the furnace was turned off. After cooling to room temperature, the reactor tube was removed for catalyst inspection, analysis, and/or replacement. The catalysts were unsupported—i.e., an inert support or carrier for the catalyst was not used in any of the runs. Except where otherwise noted, the operations were conducted using a liquid hourly space velocity (LHSV) of 0.2 hr^{-1}.

Table I summarizes the results of a number of runs at various temperatures using a variety of individual B-subgroup metal oxide catalysts in the vapor phase alkylation of aniline with diethyl ether. The reactants were employed in a ratio of 2.5 moles of diethyl ether per mole of aniline. The gasous products referred to in the tables are uncondensables and the magnitude of this figure serves as an indication of the extent of decomposition, if any, that occurred during the run. All but one of the catalysts used in these runs were obtained from commercial sources, and are identified as follows:

Catalyst No. 21—TiO_2; Harshaw Ti-X-L2873-23-10. It was of the anatase crystallographic form and had a surface area of 143 m^2/g.

Catalyst No. 22—TiO_2; Harshaw Ti-0720. It was of the anatase crystallographic form and had a surface area of 112 m^2/g.

Catalyst No. 36—TiO_2; Harshaw **[**Ti-X-L2873-23-10.**]** *Ti-X-649-84-1.* It was of the anatase crystallographic form and had a surface area of 153 m^2/g.

Catalyst No. 40—ZrO_2; Harshaw Zr-0304. It had a surface area of 46.1 m^2/g.

Catalyst No. 44—ZnO; Harshaw Zn 0701.

Catalyst No. 45—Ti_2O_3; Cerac, Inc. T-1157. It had a surface area of 0.2 m^2/g.

Catalyst No. 56—TiO; Cerac, Inc. T-1154. It had a surface area of less than 0.1 m^2/g.

The other catalyst referred to in Table I was synthesized as reported in Example 1.

EXAMPLE 1

Preparation of Catalyst No. 24—TiO_2

Titanium isopropoxide (155.15 g) was dissolved in 200 mL of isopropanol and heated to 60° C. with stirring. Distilled water (42.5 mL) was added dropwise maintaining the temperature below 70° C. to precipitate titania. Excess isopropanol was evaporated off under a dry nitrogen stream at 50°-60° C. to give a thick paste. The paste was extruded through a 50 cc plastic syringe and air-dried overnight. The extrusions were oven-dried at 110° C. for 2 hours and then calcined at 450° C. overnight to give 41.7 g of finished catalyst.

TABLE I

Alkylations Using Individual B-Subgroup Metal Oxide Catalysts

Run Number	1	2	3	4	5	6	7	8	9	10	11
Catalyst	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2
Catalyst Number	21	21	22	22	36	36	36	36	24	24	24
Temperature, °C.	250	300	250	300	300	325	350	375	300	350	400
Aniline Conversion, %	54	87	69	95	59	70	71	64	38	88	68
Ether Conversion, %	18	45	19	61	22	35	54	72	9	60	99
Product Distribution, wt. percent											
N—et aniline	64.4	38.2	51.9	16.7	63.7	52.8	51.5	51.5	82.7	50.0	22.0
o-et aniline	2.6	2.0	0.9	1.4	0.7	2.3	4.9	9.8	4.1	3.5	21.1
p-et aniline	4.5	1.9	3.5	3.4	0.9	1.3	1.6	2.3	4.5	1.3	9.2
N,N—di-et aniline	11.8	18.7	12.9	6.9	17.8	17.9	13.1	7.8	5.2	20.3	1.8
2,6-di-et aniline	2.9	2.2	3.2	6.1	2.4	2.8	3.9	7.4	—	2.6	13.8
Other ring di-et anilines	7.1	17.1	12.9	22.8	8.8	13.5	15.3	11.9	—	14.2	11.8
Ring tri-et anilines	3.3	12.4	12.2	30.4	4.0	6.1	5.1	3.4	—	4.9	5.3
Others	3.3	7.6	2.5	12.3	1.6	3.2	4.5	5.9	3.5	3.2	15.0
N—alkylation, %	76.2	56.9	64.8	23.6	81.5	70.7	64.6	59.3	87.9	70.3	23.8
Ring alkylation, %	10.0	6.1	7.6	10.9	4.0	6.4	10.5	19.5	8.6	7.4	44.1
Di-, tri-, & others, %	13.7	37.1	27.6	65.5	14.4	22.8	24.8	21.2	3.5	22.3	32.1
Ratio of o-et to p-et	0.6	1.1	0.3	0.4	0.8	1.8	3.1	4.3	0.9	2.7	2.3
Gaseous products, mL/hr	5	55	0	75	20	70	200	400	25	205	600

Run Number	12	13	14	15	16	17	18	19	20	21
Catalyst	ZrO_2	ZrO_2	ZrO_2	ZrO_2	ZnO	ZnO	ZnO	ZnO	Ti_2O_3	Ti_2O_3
Catalyst Number	40	40	40	40	44	44	44	44	45	45
Temperature, °C.	300	325	350	375	325	350	375	400	300	325
Aniline Conversion, %	94	94	77	44	37	35	40	30	10	15
Ether Conversion, %	58	89	99.5	99.9	17	38	67	94	—	1
Product Distribution, wt. percent										
N—et aniline	69.1	63.4	79.5	90.5	86.4	79.8	68.5	52.7	97.9	96.3
o-et aniline	—	0.2	0.7	1.8	—	—	3.9	1.1	—	—
p-et aniline	—	0.2	0.4	0.7	—	0.4	0.4	0.1	—	—
N,N—di-et aniline	30.4	31.1	15.3	5.7	2.1	2.2	2.5	2.1	2.1	3.1
2,6-di-et aniline	—	—	—	—	—	4.0	4.0	5.5	—	—
Other ring di-et anilines	—	—	—	—	—	2.0	2.7	8.2	—	—
Ring tri-et anilines	—	—	—	—	—	—	1.2	6.8	—	—
Others	0.5	5.2	4.1	1.4	11.5	11.6	16.6	23.5	—	0.6

TABLE I-continued

Alkylations Using Individual B-Subgroup Metal Oxide Catalysts

N—alkylation, %		99.5	94.5	94.8	96.2	88.5	82.0	71.0	54.8	100.0	99.4
Ring alkylation, %		—	0.4	1.2	2.5	—	4.4	8.3	6.7	—	—
Di-, tri-, & others, %		0.5	5.2	4.1	1.4	11.5	13.6	20.5	38.5	—	0.6
Ratio of o-et to p-et		—	1.0	1.8	2.6	—	—	9.8	11.0	—	—
Gaseous products, mL/hr		320	800	1370	1570	160	340	820	1560	10	20

Run Number	22	23	24	25	26	27	28	29	30	31*	32
Catalyst	Ti_2O_3	Ti_2O_3	TiO	TiO	TiO	TiO	TiO_2	TiO_2	TiO_2	TiO_2	TiO_2
Catalyst Number	45	45	56	56	56	56	22	22	22	22	22
Temperature, C.	350	375	300	350	375	400	325	350	375	375	400
Aniline Conversion, %	23	30	7	20	29	30	95	91	86	71	65
Ether Conversion, %	1.4	9	1	5	10	18	77	93	98	76	96
	Product Distribution, wt. percent										
N—et aniline	92.5	87.0	98.8	96.8	95.3	87.8	11.5	5.1	3.3	26.5	12.0
o-et aniline	—	0.6	—	—	—	1.1	2.4	6.1	12.0	12.2	22.9
p-et-aniline	—	—	—	—	—	—	4.1	6.2	8.8	7.8	10.6
N,N—di-et aniline	6.0	6.3	1.2	3.2	3.6	3.1	3.1	0.6	0.3	2.5	0.6
2,6 di-et aniline	—	—	—	—	—	3.4	11.7	20.4	25.7	12.1	21.5
Other ring di-et anilines	—	—	—	—	—	3.6	17.1	7.9	4.4	13.8	5.6
Ring tri-et anilines	—	—	—	—	—	—	32.4	30.3	17.8	9.3	7.7
Others	1.6	6.1	—	—	1.1	0.8	17.7	23.6	27.8	15.8	19.0
N—alkylation, %	98.5	93.3	100	100	98.9	90.9	14.6	5.7	3.6	29.0	12.6
Ring alkylation, %	—	0.6	—	—	—	1.1	18.2	32.7	46.5	32.1	55.0
Di, tri-, & others, %	1.6	6.1	—	—	1.1	7.8	67.2	61.8	50.0	38.9	32.3
Ratio of o-et to p-et	—	—	—	—	—	—	0.6	1.0	1.4	1.6	2.2
Gaseous products, mL/hr	50	50	0	15	30	70	225	315	410	670	730

*The LHSV was 0.4 per hour

In another group of runs the vapor phase alkylation of aniline with diethyl ether was performed in the same manner using various catalysts composed of two different metal oxides, one or both of which was a B-subgroup metal oxide. One of these mixed metal oxide catalysts was obtained from a commercial source. The others were prepared by me.

The commercial catalyst, Catalyst No. 50, was a mixed ZrO_2-TiO_2 catalyst from Cerac, Inc., Z-1079. It had a surface area of less than 0.1 m^2/g.

Examples 2 through 8 describe the procedures used by me in synthesizing the mixed metal oxide catalysts.

EXAMPLE 2

Preparation of Catalyst No. 19—TiO_2-5% MoO_3

155.25 Grams of titanium isopropoxide was dissolved in 200 mL of isopropanol and the solution was heated to 60° C. with stirring. Distilled water (42.5 mL) was added dropwise while maintaining the temperature below 70° C. to precipitate titania. Then 6.15 mL of a 10% aqueous solution of $(NH_4)_2MoO_4$ was added and excess solvent evaporated off under a dry nitrogen stream at 60° C. The damp precipitate was moistened with distilled water to give a thick paste. This was extruded through a 50 cc plastic syringe. The extrusions were air-dried, then oven-dried for three hours at 110° C., and then calcined overnight at 450° C. to give 43.5 g of finished catalyst.

EXAMPLE 3

Preparation of Catalyst No. 25—TiO_2-10% MoO_3

A solution made from 155.25 g of titanium isopropoxide and 200 mL of isopropanol was heated to 60° C. with stirring. Distilled water (42.5 mL) was added dropwise while maintaining the temperature below 70° C. to precipitate titania. Then 12.3 mL of a 10% aqueous solution of $(NH_4)_2MoO_4$ was added with stirring and excess solvent evaporated off under a dry nitrogen stream at 50°-60° C. to give a thick paste. This was extruded through a 50 cc plastic syringe. The extrusions were air-dried for two hours, then oven-dried overnight at 100° C., and then calcined for eight hours at 450° C. to give 43.8 g of finished catalyst.

EXAMPLE 4

Preparation of Catalyst No. 26—TiO_2-5% WO_3

A solution of 77.63 g of titanium isopropoxide in 100 mL of isopropanol was heated to 60° C. with stirring. Distilled water (21.3 mL) was added dropwise while maintaining the temperature below 70° C. to precipitate titania. Then 12.35 g of a 10% aqueous solution of $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ was added with stirring. Excess solvent was evaporated off under a dry nitrogen stream at 50°-60° C. to give a nearly dry powder. To this was added water to give a thick paste which was extruded through a 50 cc plastic syringe. The extrusions were air-dried for four hours, then oven-dried for three hours at 100° C., and then calcined at 450° C. overnight to give 22.7 g of finished catalyst.

EXAMPLE 5

Preparation of Catalyst No. 27—TiO_2-5% Fe_2O_3

A solution of 77.63 g of titanium isopropoxide in 100 mL of isopropanol was heated to 60° C. with stirring. Distilled water (21.3 mL) was added dropwise while maintaining the temperature below 70° C. to precipitate titania. To this slurry was added 53.16 g of a 10% aqueous solution of $Fe(NO_3)_3.9H_2O$ with stirring. Excess isopropanol and water were evaporated off by means of a dry nitrogen stream at 50°-60° C. to give a thick paste. Extrusions of the paste through a 50 cc plastic syringe were air-dried overnight, oven dried at 100° C. for four hours, and then calcined at 450° C. for four hours. This yielded 22.8 g of finished catalyst.

EXAMPLE 6

Preparation of Catalyst No. 32—TiO_2-10% Fe_2O_3

The procedure of Example 5 was repeated in the same fashion except that 106.32 g of the 10% aqeuous solution of $Fe(NO_3)_3.9H_2O$ was added to the titania slurry. During the stripping at 50°-60° C., the solids began to granulate and turn dark brown before all of the isopropanol has been removed. This experiment yielded 22.3 g of a dense, black finished catalyst.

EXAMPLE 7

Preparation of Catalyst No. 35—TiO_2-20% Fe_2O_3

A solution of 77.63 g of titanium isopropoxide in 100 mL of isopropanol was heated to 60° C. with stirring. Distilled water (21.3 mL) was added dropwise while maintaining the temperature below 70° C. to precipitate titania. To this slurry was added 100 g of a 21.26 wt % aqueous solution of $Fe(NO_3)_3.9H_2O$ with stirring. Excess isopropanol and water were evaporated off by means of a dry nitrogen stream at 40°-50° C. to give a thin paste. Further evaporation of water was conducted at low heat with a hot plate to give a thick paste. The paste was oven-dried at 100° C. overnight. The resulting large particles were crushed to less than 2 mm, then calcined at 450° C. for six hours to give 26.0 g of finished catalyst.

EXAMPLE 8

Preparation of Catalyst No. 38—TiO_2-10% Fe_2O_3

The procedure of Example 5 was repeated in the same manner except that 10.63 g of $Fe(NO_3)_3.9H_2O$ in 50 mL of water was used. After removing the excess solvent the thick paste of the catalyst was poured onto a flat surface and air-dried, then oven-dried at 100° C. overnight. Calcining at 450° C. for six hours gave 23.4 g of finished catalyst.

TABLE II

Alkylations Using Two Metal Oxides One or Both Being a B-Subgroup Metal Oxide Catalyst

Run Number	33	34	35	36	37	38	39	40
Catalyst	TiO_2— 5% MoO_3	TiO_2— 5% MoO_3	TiO_2— 5% MoO_3	TiO_2— 10% MoO_3	TiO_2— 10% MoO_3	TiO_2— 10% MoO_3	TiO_2— 10% MoO_3	TiO_2— 5% WO_3
Catalyst Number	19	19	19	25	25	25	25	26
Temperature, °C.	325	350	375	300	325	350	375	325
Aniline Conversion, %	82	64	65	65	60	59	34	91
Ether Conversion, %	54	63	92	55	49	57	55	64
			Product Distribution, wt. percent					
N—et aniline	52.0	51.9	23.5	62.6	63.7	54.5	46.6	45.3
o-et aniline	6.4	10.5	20.2	5.8	7.7	12.1	12.8	3.7
p-et aniline	2.0	3.3	7.4	2.6	3.1	4.7	5.2	2.2
N,N—di-et aniline	11.0	6.3	2.1	9.4	6.9	3.7	1.4	18.2
2,6-di-et aniline	3.5	4.3	11.5	3.1	2.9	3.6	3.7	1.9
Other ring di-et anilines	14.0	10.9	10.6	10.1	9.0	10.7	9.0	17.9
Ring tri-et anilines	3.7	2.6	4.0	1.8	1.2	1.7	2.4	6.7
Others	7.4	10.2	20.8	4.5	5.5	9.0	19.0	4.2
N—alkylation, %	63.0	58.2	25,6	72.0	70.6	58.2	48.0	63.5
Ring alkylation, %	11.9	18.1	39.1	11.5	13.7	20.4	21.7	7.8
Di-, tri-, & others, %	25.1	23.7	35.4	16.4	15.7	21.4	30.4	28.8
Ratio of o-et to p-et	3.2	3.2	2.7	2.2	2.5	2.6	2.5	1.7
Gaseous products, mL/hr	160	195	550	0	0	200	370	220

Run Number	41	42	43	44**	45	46	47	48
Catalyst	TiO_2— 5% WO_3	TiO_2— 5% Fe_2O_3	TiO_2— 5% Fe_2O_3	TiO_2— 5% Fe_2O_3	TiO_2— 10% Fe_2O_3	TiO_2— 10% Fe_2O_3	TiO_2— 10% Fe_2O_3	TiO_2— 20% Fe_2O_3
Catalyst Number	26	27	27	27	32	32	32	35
Temperature, °C.	350	350	375	375	300	350	375	350
Aniline Conversion, %	89	87	78	55	13	31	33	14
Ether Conversion, %	89	76	83	78	13	50	69	22
			Product Distribution, wt. percent					
N—et aniline	27.8	40.5	39.8	43.0	87.7	56.2	31.3	39.2
o-et aniline	7.7	7.7	12.0	17.9	6.4	23.4	36.4	46.6
p-et aniline	4.3	2.3	3.1	3.8	—	5.5	6.2	—
N,N—di-et aniline	7.0	10.6	6.2	3.3	0.6	1.6	1.4	—
2,6-di-et aniline	9.0	5.4	6.5	6.1	—	3.6	4.8	2.4
Other ring di-et anilines	20.3	19.7	14.1	10.5	—	6.1	5.2	3.3
Ring tri-et anilines	12.5	5.4	3.5	1.7	—	—	3.7	2.4
Others	11.3	8.4	14.9	13.8	5.3	3.7	10.9	6.0
N—alkylation, %	34.8	51.1	46.0	46.3	88.3	57.8	32.7	39.2
Ring alkylation, %	21.0	15.4	21.6	27.8	6.4	32.5	47.4	49.0
Di-, tri-, & others, %	44.1	33.5	32.5	26.0	5.3	9.8	19.8	11.7
Ratio of o-et to p-et	1.8	3.4	3.9	4.7	—	4.3	5.9	—
Gaseous products, mL/hr	475	295	415	460	15	450	690	190

Run Number	49	50	51	52	53	54	55	56	57
Catalyst	TiO_2— 20% Fe_2O_3	TiO_2— 10% Fe_2O_3	TiO_2— 10% Fe_2O_3	TiO_2— 10% Fe_2O_3	TiO_2— 10% Fe_2O'	ZrO_2— TiO_2	ZrO_2— TiO_2	ZrO_2— TiO_2	ZrO_2— TiO_2
Catalyst Number	35	38	38	38	38	50	50	50	50

TABLE II-continued

Alkylations Using Two Metal Oxides One or Both Being a B-Subgroup Metal Oxide Catalyst

Temperature, °C.	375	300	350	375	400	300	350	375	400
Aniline Conversion, %	18	30	66	57	41	1	15	14	11
Ether Conversion, %	50	10	65	78	90	5	18	13	15
				Product Distribution, wt. percent					
N—aniline	20.6	87.3	57.1	46.8	33.4	100	95.9	88.7	81.2
o-et aniline	56.8	1.5	9.1	16.1	25.6	—	—	—	0.7
p-et aniline	1.0	0.2	1.6	3.2	6.0	—	—	—	—
N,N—di-et aniline	—	5.5	7.8	3.0	1.0	—	2.8	1.8	1.0
2,6 di-et aniline	3.9	1.3	4.7	5.5	4.2	—	—	—	—
Other ring di-et anilines	4.9	2.3	11.5	9.6	8.9	—	—	—	—
Ring tri-et anilines	3.2	0.1	2.3	2.9	4.4	—	—	—	—
Others	9.5	1.8	5.8	12.9	16.5	—	1.3	9.4	17.1
N—alkylation, %	20.6	92.8	64.9	49.8	34.4	100	98.7	90.5	82.2
Ring alkylation, %	61.7	3.0	15.4	24.8	35.8	—	—	—	0.7
Di-, tri-, & others, %	17.6	4.2	19.6	25.4	29.8	—	1.3	9.4	17.1
Ratio of o-et to p-et	56.8	7.5	6.1	5.0	4.3	—	—	—	—
Gaseous products, mL/hr	410	40	350	620	990	30	110	110	160

**Water was included in the reactant feed so that the molar ratio of H_2O aniline:ether was 5:1:2.5.

In another series of alkylations various different ether alkylating agents were used in reactions with aniline. In these experiments the following ethers were employed: tetrahydrofuran (THF), dibutyl ether (bu_2O), tetrahydropyran (THP), and 1,4-dioxane (dioxane). The results of these experiments are set forth in Table III.

TABLE III

Alkylations Using Other Ether Akylating Agents

Run Number	58	59	60	61	62	63
Alkylating Agent	THF	Bu_2O	Bu_2O	THF	THP	Dioxane
Catalyst Number	19	19	19	22	22	22
Temperature, °C.	350	350	400	250	300	300
Etheraniline mole ratio	3:1	1:1	1:1	3:1	3:1	2:1
Aniline Conversion, %	91	36	30	98	74	32
Ether Conversion, %	83	66	96	43	46	24
		Product Distribution, wt. percent				
N—ET aniline						19.0
o-et aniline						5.6
p-et aniline						16.1
N,N—di-et aniline						—
2,6-di-et aniline						3.9
Other di-et anilines						11.9
Ring bu anilines			25.7			
N—bu aniline	1.7	24.8	20.6			
1-phenyl pyrrole	5.0					
1-phenyl pyrrolidine	65.0			96.8		17.8
1-phenyl piperidine					97.9	
Others	28.3	75.2	53.7	3.2	2.1	25.6
N—alkylation, %						19.0
Ring alkyation, %						25.6
Di-, tri- & others, %						55.3
Ratio of o-et to p-et						0.3
Gaseous products, mL/hr						100

Table IV summarizes the results of additional runs in which N-ethylaniline was alkylated with diethyl ether (Runs 64–68) and 2,6-diethylaniline was alkylated with dimethyl ether (Runs 69–70) using several different catalysts based on titanium dioxide. In Runs 64–68, the reactants were fed in a ratio of 2 moles of the ether per mole of the aniline reactant. In Runs 69 and 70 this ratio was 2.5 to 1.

TABLE IV

Alkylations of Substituted Anilines

Run Number	64	65	66	67	68	69	70
Catalyst Number	24	24	19	19	32	21	21
Temperature, °C.	350	400	350	400	375	250	300
Amine Conversion %	30	51	63	88	39	43	86
Ether Conversion, %	54	93	71	98	40		
		Product Distribution, wt. percent					
Aniline	5.1	19.8	25.6	48.4	33.0		
N—et aniline	69.5	*48.6* [48.5]	37.5	12.5	60.6		
o-et aniline	1.7	5.9	4.4	11.7	1.6		
p-et aniline	0.9	3.1	1.7	6.4	0.2		
N,N—di-et aniline	12.4	4.9	6.1	0.9	1.2		
2,6-di-et aniline	0.8	2.2	1.7	3.1	0.4		
Other di-et anilines	6.3	8.3	6.7	4.1	1.0		
4-me-2,6-di-et aniline							2
N—me-2,6-di-et aniline						42	13
N,N—di-me-2,6-di-et aniline						58	26
N,4-di-me-2,6-di-et aniline							15
N,N,4-tri-me-2,6-di-et aniline							44
Others	3.3	7.2	16.3	12.9	1.9		
N—alkylation, %	12.4	4.9	6.1	0.9	1.2	100	39
Ring alkylation, %	3.4	11.2	7.8	21.2	2.2		61
Di-, tri- & others, %	9.2	15.5	23.0	17.0	3.0		
Ratio of o-et to p-et	1.9	1.9	2.6	1.8	8.0	—	120
Gaseous products, mL/hr	200	140	360	710	330		

In contrast to the results reported above, extensive amounts of decomposition of the alkylating agent were encountered when using an alcohol as the alkylating agent and an iron oxide-germanium oxide catalyst in accordance with the prior art. See in this connection U.S. Pat. No. 4,351,958. In particular, when ethanol and aniline were reacted in the above manner at 350 C over a catalyst composed of 96.1 weight percent Fe_2O_3 and 3.9 weight percent GeO_2, non-condensable gases were evolved at the rate of 1800 mL/hr. In fact, no ethanol passed through the reaction zone—the ethanol which did not react with the aniline was completely destroyed.

As noted above, the inclusion of water in the feed to the catalyst can be helpful insofar as the regiochemical aspects of the process are concerned. For example a comparison of Runs 43 and 44 in Table II shows that the presence of water resulted in an increase in the ratio of o-ethylaniline to p-ethylaniline from 3.9 to 4.7. When water is employed, it will normally be used in amounts no higher than about 10 moles per mole of ether used, preferably in amounts falling in the range of about 0.1 to about 5 moles per mole of ether used.

An extensive series of N,N-cyclodialkylation reactions of this invention was carried out using Catalyst No. 22, and the tubular reactor and vapor phase reaction procedure described above. The reaction conditions used and results obtained are summarized in Table V. All conversions shown in Table V are based on the amines/amide except as otherwise indicated.

TABLE V

Gem Cyclodialkylation of Amines and Amides

Run No.	Reactants	Molar Ratio*	Temp °C.	Conversion, %	Product Yield, %	Products(s)
71	Tetrahydrofuran & Aniline	3:1	300	98	92	1-Phenylpyrrolidine
72	Tetrahydrofuran & Aniline	3:1	250	98	97	1-Phenylpyrrolidine
73	Tetrahydropyran & Aniline	3:1	300	74	98	1-Phenylpiperidine
74	Furan & Aniline	3:1	250	70	99	1-Phenylpyrrole
75	Tetrahydrofuran & Methylamine	1:1	300	42**	100	1-Methylpyrrolidine
76	Tetrahydrofuran & n-Butylamine	2:1	300	14	41	1-Butylpyrrolidine
77	2,5-Dihydrofuran & Methylamine	2:3	250	15**	43	1-Methylpyrrolidine
78	*2,3-Dihydrofuran* [2,5-Dihydrofuran] & Methylamine	1:1	275	26**	64 8	1-Methylpyrrolidine 1-Methylpyrrolidine
79	*Dihyrdopyran* [Dihydrofuran] & Aniline	3:1	250	31	43	1-Phenylpiperidine
80	2,5-Dimethyltetrahydrofuran & Aniline	3:1	250	70	88	1-Phenyl-2,5-dimethylpyrrolidine
81	Tetrahydrofuran & 2,6-Diethylaniline	3:1	250	69	96	1-(2,6-Diethylphenyl)pyrrolidine
82	Tetrahydrofuran & N—methylaniline	3:1	305	95	65	1-Phenylpyrrolidine
83	Gamma-Butyrolactone & Aniline	3:1	200	93	97	1-Phenyl-2-pyrrolidone
84	Furfuryl alcohol & Aniline	3:1	225	57	10 55	1-Phenyl-2-hydroxymethylpyrrole 1-Phenyl-2-methylpyrrole
85	Tetrahydrofurfuryl alcohol & Aniline	3:1	300	37	58	1-Phenylpiperidine
86	2-Methoxytetrahydrofuran & Aniline	2:1	225	45	70	1-Phenylpyrrolidine
87	Furfuryl amine & Aniline	2:1	325	8	15 5 6	1-Phenyl-2-methylpyrrole 1-Phenyl-2-methylpyrrolidine 1-Phenylpyrrole
88	2-Furaldehyde & Aniline	2:1	350	20	5 4	1-Phenylpyrrole 1-Phenyl-2-methylpyrrole
89	Tetrahydrofuran & Acetamide	2:1	200	76	45	1-Acetylpyrrolidine
90	Tetrahydrofuran & o-Anisidine	2:1	275	30	9 26	1-(2-Methoxyphenyl)pyrrolidine 1-(2-Hydroxyphenyl)pyrrolidine
91	Tetrahydrofuran & Anthranilonitrile	2:1	250	6	43 57	1-(2-Cyanophenyl)pyrrolidine 1-Phenylpyrrolidine
92	Tetrahydrofuran & o-Chloroaniline	2:1	250	5	59 35	1-(2-Chlorophenyl)pyrrolidine 1-Phenylpyrrolidine
93	3-Hydroxytetrahydrofuran & Methylamine	***	275	12**	61 38	1-Methylpyrrol 1-Methylpyrrolidine
94	Tetrahydrofuran & Methylenebis Aniline	6:1	300	100	44 27	1-Phenylpyrrolidine 1-(p-Tolyl)pyrrolidine

*Cyclic ether:Amine/Amide
**Based on the cyclic ether
***Not known

It will be noted that in Run 85, a ring expansion occurred during the course of the N,N-cyclodialkylation reaction. See in this connection, J. Chem. Soc., Section B, 1970, 1525-27, which reports that reaction of ammonia with tetrahydrofuryl alcohol over a palladium-/alumina catalyst at 300° C. gave 1,2,3,4-tetrahydropyridine.

Example 9 illustrates the use of a liquid phase batch type operation in the practice of this invention. Additionally, it shows the applicability of the N,N-cyclodialkylation reaction to an unstrained cyclic ether having a heterocyclic nitrogen atom in the ring.

EXAMPLE 9

[Bynthesis] *Synthesis* of N-Phenylimidazolidone

Aniline (15.40 g; 0.165 mole) and 2-oxazolidone (9.60 g; 0.110 mole) were refluxed for 6.5 hours with 1.00 g (0.0125 mole) of titanium dioxide (Harshaw Ti 0720 which had been calcined at 300° C. for 4 hours). The reaction mass was cooled to 0° C. and the crystals which had formed were filtered off. The crystals were recrystallized from ethanol to give N-phenylimidazolidone in 47% yield. The conversion based on 2-oxazolidone was 99%.

Liquid phase or vapor phase procedures similar to those described in the above examples may be used in connection with other suitably reactive cyclic ethers containing one or more hetero atoms other than oxygen.

The conditions used in the process of this invention are susceptible to considerable variation. For example, while my process is usually conducted with an excess of the ether reactant relative to the aromatic amine reactant, a stoichiometric deficiency of the ether may be used, especially when seeking to maximize monoalkylation and minimize polyalkylation. Likewise, the ratio used will be influenced to some extent by the composition of the amine (i.e., whether it is a monoamine or a polyamine), the composition of the ether (i.e., whether it is a monoether or a polyether), and the extent and type of alkylation (i.e., nuclear alkylation and/or N-alkylation) desired. In most cases, the reaction mixture will contain about 0.5 to about 5 molar equivalents of the ether per molar equivalent of the amine. In the case of reactions between monoethers and monoamines, the molar ratio of ether to amine is preferably in the range of about 1:1 to about 3:1.

It is possible to vary certain aspects and other features of the above described invention without departing from the lawful scope or true spirit thereof.

I claim:

1. The process of converting an N,N-dialkylatable amino or amido group into an N,N-cyclodialkylated amino or amido group which comprises reacting a compound containing at least one N,N-dialkylatable amino or amido group with an unstrained cyclic ether co-reactive therewith in the presence of a viable B-subgroup metal oxide alkylation catalyst other than a Group I-B metal oxide so that at least one such N,N-dialkylatable amino or amido group is transformed into an N,N-cyclodialkylated amino or amido group, respectively[.], *such that when said group being transformed in an amino group, said cyclic ether has a furan ring system, a dihydrofuran ring system, a pyran ring system or a dihydropyran ring system.*

[**2.** A process of claim **1** wherein the ether has a single oxygen atom and at least four carbon atoms in the ring.]

3. A process of claim **1** wherein said compound has at least one N,N-dialkylatable primary amino group in the molecule.

4. A process of claim **1** wherein the reaction is conducted in the vapor phase by contacting a vapor phase mixture of the reactants with a bed of the catalyst.

5. A process of claim **1** wherein the reaction is conducted in the liquid phase in the presence of the catalyst.

6. A process of claim **1** wherein the reaction is conducted at a temperature of at least about 200° C. but below that at which the catalyst becomes inactive.

7. A process of claim **1** wherein the catalyst is composed predominantly or entirely of one or more oxides of one or more Group IV-B metals.

8. A process of claim **7** wherein the catalyst is composed predominantly or entirely of titanium dioxide.

9. The process of converting an N,N-dialkylatable amino group into an N,N-cyclodialkylated amino group which comprises reacting a compound containing at least one N,N-dialkylatable amino group with an unstrained cyclic ether co-reactive therewith in the presence of a viable B-subgroup metal oxide alkylation catalyst other than a Group I-B metal oxide at a temperature of at least about 200° C. but below that at which the catalyst becomes inactive, so that at least one such N,N-dialkylatable amino group is transformed into an N,N-cyclodialkylated amino group[.], *said cyclic ether having a furan ring system, a dihydrofuran ring system, a pyran ring system or a dihydropyran ring system.*

[**10.** A process of claim **9** wherein the ether has but a single ring composed of a furan ring system, a dihydrofuran ring system, a tetrahydrofuran ring system or a dihydropyran ring system.]

11. A process of claim **9** wherein said compound has at least one N,N-dialkylatable primary amino group in the molecule.

12. A process of claim **11** wherein said compound is a primary aromatic amine.

13. A process of claim **12** wherein the amine is a mononuclear primary aromatic amine having one or two amino groups on one or two aromatic rings.

14. A process of claim **11** wherein said compound is a primary aliphatic amine.

15. A process of claim **14** wherein said amine is a monoalkyl amine.

16. A process of claim **9** wherein the catalyst is composed predominantly or entirely of a dioxide of one or more Group IV-B metals.

17. A process of claim **16** wherein the ether is furan, a dihydrofuran, [tetrahydrofuran, a mono- or polyalkyl substituted tetrahydrofuran,] furfuryl alcohol, a dihydrofurfuryl alcohol, [tetrahydrofurfuryl alcohol, an alkoxytetrahydrofuran, a hydroxytetrahydrofuran,] furaldehyde, furfurylamine,*or* dihydropyran[, or tetrahydropyran.].

18. A process of claim **17** wherein said compound is a primary aromatic amine or a primary aliphatic amine.

19. A process for the production of imidazolidones which comprises heating a compound containing at least one N,N-dialkylatable primary amino group with an oxazolidone in the presence of a viable catalyst consisting essentially of a dioxide of at least one Group IV-B metal so that N,N-cyclodialkylation of the amino group takes place.

20. A process of claim **19** wherein said compound is a primary aromatic or aliphatic amine, said oxazolidone is 2-oxazolidone and said catalyst consists essentially of titanium dioxide.

21. A process for the production of N,N-cyclodialkylated amines which comprises reacting N,N-cyclodialkylatable [primary or] secondary aliphatic amine or N,N-cyclodialkylatable [primary or] secondary aromatic amine with an unstrained cyclic ether co-reactive therewith in the presence of a viable B-subgroup metal oxide catalyst other than a group I-B metal oxide at a temperature of at least about 200° C., but below that at which the catalyst becomes inactive, so that N,N-cyclodialkylated amine is produced.

22. A process of claim **21** [wherein the amine used in the reaction is a primary alkyl amine or a primary aromatic amine,] wherein the ether has but a single ring composed of a furan ring system, a dihydrofuran ring system, a tetrahydrofuran ring system, or a dihydropyran ring system and wherein the catalyst is composed predominantly or entirely of titanium dioxide or zirconium dioxide.

23. A process of claim **22** wherein the reaction is conducted in the vapor phase by contact a vapor phase mixture of the reactants with a bed of the catalyst.

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