Table IV. Hydrolytic Stability of Ethers Derived from Chloromethylated Diphenyl Ethers

Run No.	*Composition*		*Cu. Wt. Loss, Mg./Sq. Cm.*	*Water Layer Total Acidity, Mg. KOH*	*Organic Layer, Acid No.*	*Treatment*
	CMDPO	*Alcohol*				
MIL H-19457A	..	...	0.3 max.	5.0 max.	0.2 max. increase	...
2	17	$H(CF_2)_4CH_2OH$	0.15	5.76	0.01	Activated charcoal only
7A, 7B	25	$H(CF_2)_2CH_2OH$	0.023	1.17	0.08	Base treatment followed by activated charcoal
8	25	$H(CF_2)_4CH_2OH$	0.031	0.86	0.01	Base treatment followed by activated charcoal
11	32	$H(CF_2)_2CH_2OH$	0.106	12.1	0.04	Activated charcoal only
24	Di	$H(CF_2)_4CH_2OH$	0.03	0.75	0.01	Redistilled, followed by activated charcoal

These facts unequivocally proved that the fluoroalkyl ethers of this paper are hydrolytically stable.

Self-condensation of the chloromethyl compounds is the cause for relatively low yields observed in many cases. Thus, relatively high increases in pressures were encountered frequently during the distillation and large amounts of distillation bottoms were obtained. That these phenomena were not caused by instability of the ethers themselves was conclusively shown by the fact that the ethers could be redistilled without any indication of decomposition.

Uses

It is anticipated that these fluids, after proper formulation, could find many industrial applications, particularly where fire resistance is of concern. Potential uses as industrial hydraulic fluids, compressor fluids, heat transfer fluids, and hydraulic fluids in the automotive, aviation, and naval sector are indicated.

Acknowledgment

We are indebted to S. A. Kolbeck for technical assistance.

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PREPARATION OF DIMETHYLMORPHOLINE BY REACTION OF DIPROPYLENE GLYCOL WITH AMMONIA

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Dimethylmorpholine is prepared by the catalytic reaction of commercial dipropylene glycol with ammonia. Conversions of above 65% and yields of about 80% are attained by passing the vaporized glycol with ammonia and hydrogen over a bed of 60% nickel-on-kieselguhr catalyst. The product produced from commercial dipropylene glycol is a mixture of 2,5- and 3,5-dimethylmorpholines. Typically, the process is carried out by feeding a vaporized mixture of dipropylene glycol, water, hydrogen, and ammonia in a mole ratio of 1:1:3:5 over the catalyst at 190° C. and at a feed rate corresponding to 0.1 gram per gram of catalyst per hour. In addition to dimethylmorpholine, the condensed effluent from the reaction contains unsaturated cyclics which are converted to dimethylmorpholine by catalytic hydrogenation.

THE development of a process for preparing morpholines by the reaction of ammonia with dialkylene glycols (*2*) is one phase of a general program carried out in our laboratories on the synthesis of heterocyclic nitrogen compounds by catalytic cycloamination (*3–5*). This reaction provides a direct method for preparing a morpholine in the form of the free base. In contrast, the conventional commercial process for making morpholine consists in dehydrating diethanolamine with concentrated sulfuric acid and treating the morpholine sulfate with a strong base. The direct process uses lower cost raw materials and potentially has a lower manufacturing cost.

Dimethylmorpholine Isomers

The major effort was devoted to the preparation of dimethylmorpholine from dipropylene glycol. The commercial grade of dipropylene glycol is a mixture of two isomers, approximately 70% 2-(2-hydroxypropoxy)-1-propanol and 30% 1,1′-oxydi-

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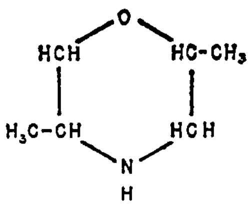
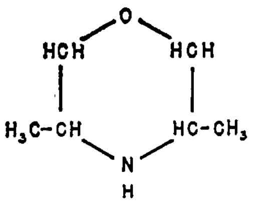
2-propanol. Therefore, the cycloamination product is a mixture of 2,5- and 3,5-dimethylmorpholine isomers.



2,5-DIMETHYLMORPHOLINE



3,5-DIMETHYLMORPHOLINE

As a result of the saturated ring system, each of these position isomers of dimethylmorpholine will have the possibility of cis and trans forms, giving in all a mixture of four species. The presence of asymmetric carbon atoms at the substituted ring positions will, of course, result in a series of optical isomers. Only the position isomers were considered in the present work.

Physical properties of a typical mixed isomer product and of the individual isomers are given in Table I.

Experimental

Isolation and Analysis of Products. Conversions and yields to morpholines, as used in the following discussion, have the following meanings:

$$\% \text{ conversion} = \frac{\text{moles of product} \times 100}{\text{moles of dialkylene glycol charged}}$$

$$\% \text{ yield} = \frac{\text{moles of product} \times 100}{\text{moles of dialkylene glycol charged} - \text{moles recoverable}}$$

For analysis, aliquots of the crude reaction products were fractionally distilled through a 120 × 2.8 cm. electrically heated distillation column packed with $^1/_8$-inch glass helices. Water in the crude product was removed by azeotropic distillation with benzene, and after the benzene and a small intermediate fraction had been distilled off, the dimethylmorpholine fraction was collected over the range of 140° to 150° C. The dimethylmorpholine fraction was weighed and analyzed by titration with standard HCl. Dipropylene glycol was recovered by distillation at 20 mm. of Hg pressure.

Procedure for Liquid-Phase Cycloamination of Dipropylene Glycol. Liquid-phase experiments were conducted either in a 1-gallon stainless steel stirred autoclave having a 1200-p.s.i.g. operating pressure (manufactured by Autoclave Engineers, Inc.) or in a 1.5-liter rocking bomb having a 5000-p.s.i.g. working pressure (manufactured by American Instrument Co.). Raney nickel catalyst drained of excess water was washed from a beaker into the autoclave with the feedstock. After the ammonia had been charged, hydrogen was added to give an initial pressure of 50 p.s.i.g. in the case of the stirred autoclave, or 200 p.s.i.g. in the case of the rocking bomb. The charge was heated to the predetermined temperature, and the pressure was adjusted to the desired working pressure by addition of more hydrogen. At the end of the reaction period, the charge was cooled and the autoclave was vented slowly to relieve the hydrogen and ammonia pressure. The contents were then drawn off, filtered, and distilled.

Procedure for Vapor-Phase Cycloamination of Dipropylene Glycol. The apparatus for vapor-phase reactions consisted of a metering pump for delivering reactant continuously at a fixed measurable rate, a preheater section, a heated catalyst chamber, and a condenser system. An electrically heated iron-core furnace was used for the first series of runs (Table III). Because of inherent difficulties in temperature control, a Dowtherm-heated reactor (Figure 1) was used for the remainder of the investigation.

The reactor, *D*, consists of a 1-inch steel pipe 72 inches long surrounded by a 60-inch Dowtherm jacket. Heat is supplied by Chromel-ribbon heating elements and the reactor is insulated with magnesia lagging. The level of the Dowtherm used as the heat transfer medium is adjusted to be above the catalyst bed, *H*. The electrical heating elements located below the Dowtherm level are used to boil the Dowtherm, the corresponding pressure being measured on the pressure gage, *L*. Dowtherm vapor is condensed by the condenser, *K*, and returned to the jacket through the sight glass, *N*. Emergency protection against excessive pressure is provided by the safety head, *M*. The temperatures of the Dowtherm liquid and the temperatures throughout the reactor section are measured by thermocouples at three sites, *F*. In addition to the inlet for liquid feed at the top of the reactor, a second inlet for gases, *C*, is provided. The feed system consists essentially of a graduated feed reservoir, *A*, and a proportioning pump, *B*, for delivering the liquid feed to the top of the reactor. A buret, *O*, is used to calibrate the feed rate. By closing the valve at the bottom of the reservoir and feeding from the buret, *O*, accurate volume readings can be obtained. A mercury manometer, *J*, attached to the feed line measures the back pressure in the system and also serves as a safety head.

The catalyst bed was positioned in the reactor as shown in Figure 1. Hydrogen addition was started before heating the reactor. After desired reaction temperature was reached, ammonia flow was started and adjusted. Finally, feed of

Table I. Properties of Dimethylmorpholine

	Boiling Point,[a] *° C., 750 mm.*	*Refractive Index,* n_D^{25}	*Density,* d_4^{16}
Mixed isomer	142–147	1.4424	0.933
2,5 isomer	145–146	1.4421	0.936
3,5 isomer	143–144	1.4413	0.931

[a] *Uncorrected.*

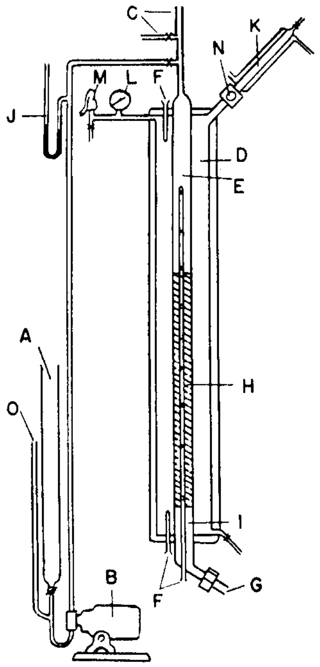


Figure 1. Vapor phase reactor system

- A. Graduated food reservoir
- B. Pump
- C. Gas inlet
- D. Dowtherm heated reactor
- E. Inert packing (preheat)
- F. Thermocouple wells
- G. To condenser
- H. Catalyst section
- I. Inert packing
- J. Safety valve and gage
- K. Dowtherm condenser
- L. Dowtherm pressure gage
- M. Safety head
- N. Sight glass
- O. Buret

dipropylene glycol was begun. A liquid ammonia reflux was maintained at the receiver exit in order to minimize vapor entrainment loss of product.

At the beginning of a run, the feed reservoir was charged to the zero mark and the receiver was emptied. At the end of the run, the feed reservoir was refilled to the zero mark and the effluent collected in the receiver was simultaneously drained and weighed. The weight of feed stock necessary to refill the reservoir was taken as the charge for the run. Condensed products were fractionally distilled and analyzed by the procedure described for products prepared by the liquid-phase procedure.

Results and Discussion

Liquid-Phase Process. Earlier work (*4*) had shown that 2,6-dimethylpiperazine is prepared in 80% conversion by the liquid-phase reaction of diisopropanolamine (*N,N'*-imino-bis-2-propanol) with ammonia in the presence of Raney nickel catalyst at a temperature of 190° C. and a pressure of about 1000 p.s.i.g. Therefore, similar conditions were selected for experiments on the synthesis of dimethylmorpholine from dipropylene glycol (Table II).

The first three runs were conducted in the 1-gallon stainless steel autoclave, with ammonia charged as a 28% aqueous solution. The last two experiments were conducted in the rocking bomb autoclave using anhydrous ammonia.

The reactivity of dipropylene glycol was found to be much less than of diisopropanolamine. The conversion to dimethylmorpholine was only 31% after a 24-hour reaction time at 220° C. and 2350-p.s.i.g. pressure. Even though the yield might ultimately be much higher than 31% by using still longer reaction times and recycling dipropylene glycol, the liquid-phase approach appeared to be unattractive as a potential commercial process. At such a low production rate, the capital investment for the necessary high pressure equipment would be excessive. Therefore, the liquid-phase approach was abandoned and potentially lower cost continuous vapor-phase methods were investigated.

Vapor-Phase Process. The major variables in a vapor-phase process are temperature, ratio of reactants, space velocity, catalyst type, and catalyst age. Previous experience on the amination of glycol ethers (*7*) had shown Ni 0104 T 1/8 (60% nickel-on-kieselguhr catalyst manufactured by the Harshaw Chemical Co.) to be an excellent amination catalyst. Therefore, after initial runs on the cycloamination of dipropylene glycol proved successful, this catalyst was used exclusively, and catalyst type was eliminated as a variable. Also, because of previous experience with this type of reaction, satisfactory conversions and yields were attained with a smaller number of experiments than normally would have been required. Thus, in the second experiment, a conversion of 65% and a yield of 81% were achieved. Therefore, the major portion of the investigation was directed toward variations of the reaction conditions around those of that experiment, and toward determining the effect of the age of catalyst upon conversion and yields.

Table II. Liquid-Phase Amination of Dipropylene Glyco

Raney nickel catalyst, 10 g./mole of dipropylene glycol

Run No.	*Charge* Glycol, moles	*Charge* NH_3, moles	*Pressure, P.S.I.G.*	*Temp., ° C.*	*Time, Hr.*	*Conv., %*
1	6.0	18.0	780	220	7.5	0.0
2	6.0	18.0	1200	240	5.0	5.0
3	7.0	22.2	1200	180	4.0	1.5
4	5.0	15.0	2350	220	4.0	8.4
5	5.0	15.0	2350	220	24	31

Although samples of crude dimethylmorpholine assayed 98% on the basis of neutral equivalent, on storage they developed color and, when redistilled, as much as 10% of tarry residue was obtained. The impurity was found to be a material which was readily convertible to dimethylmorpholine by hydrogenation. While the proof is not unequivocal, all experimental evidence indicates that the offending impurity is a cyclic Schiff base which actually may be a precursor to dimethylmorpholine in the synthesis. Limited studies showed that the unsaturated material is converted completely to dimethylmorpholine by catalytic hydrogenation.

The exploratory runs in Table III were carried out over 10- to 17-hour reaction periods, a fresh charge of catalyst being used for each run. One mole of water per mole of dipropylene glycol was used to moderate the high initial activity of the catalyst.

The data show that a temperature of >185° C. is needed to obtain conversions of 60% or greater, and additional study of the effect of temperature indicated that 190° to 195° C. was approximately the optimum temperature. The experiments made at 190° to 195° C. show that feed ratios of 2.5 to 7.5 moles of ammonia and 2.5 to 4.0 moles of hydrogen per mole of dipropylene glycol are in a satisfactory range. The requirement of at least some hydrogen is strikingly revealed by Experiment 6, in which no hydrogen was used. The conversion was only 19% after the first 17 hours of operation and, after an additional 24 hours, the catalyst was completely inactive.

The effect of space velocity was investigated at 190° and 200° C. on the same bed of catalyst over a total time of 42 hours. The term space velocity, as used in this work, is an arbitrary function of the ratio of the total feed volume per hour as gases at 0° C. to the volume of the catalyst.

$$\text{Space velocity, hr.}^{-1} = \frac{\text{total moles of feed/hr.} \times 22{,}400 \text{ ml./mole}}{\text{volume of catalyst zone, ml.}}$$

The above definition, of course, does not consider the increase in volume of the gases at reaction temperature or the volume of the catalyst pellets and, thus, is not suitable for estimation of the contact time. However, it was considered adequate for estimating the effect of the total feed rate.

Table III. Vapor-Phase Amination of Dipropylene Glycol

Harshaw Ni 0104 catalyst, 325 ml. (approx. 450 g.)

Run No.	*Temp., ° C.*	*Relative Space Velocity*	*Feed Rate, Moles/Hour* Glycol	*Feed Rate, Moles/Hour* NH_3	*Feed Rate, Moles/Hour* H_2	*Conv., %*	*Yield, %*
1	180–185	370	0.6	3.0	1.8	58	68
2	190–195	370	0.6	3.0	1.8	65	81
3	190–195	340	0.4	3.0	1.6	68	78
4	190–195	240	0.6	1.5	1.5	65	72
5	180–185	390	0.75	3.0	1.87	50	61
6	180–185	250	0.6	3.0	0.0	19	43

Data given in Table IV show a decrease in conversion from 78 to 64% at 190° C. and from 75 to 65% at 200° C. when the space velocity is doubled. Little effect on the yield was observed. The higher space velocity would result in an increased production rate, but this could be offset by the cost of recovering and recycling dipropylene glycol. The effect of increased space velocity on catalyst life was not studied.

In order to determine if the constituent isomers of commercial dipropylene glycol react differently in the cycloamination reaction and, additionally, to obtain samples of the individual morpholine isomers for analytical standards, vapor-phase cycloaminations were made with 1,1′-oxydi-2-propanol and 2-(2-hydroxypropoxy)-1-propanol, which were prepared by published methods (*6*).

Conversions and yields given in Table V show little significant difference in the cycloamination rates of these isomeric dipropylene glycols.

The results of a catalyst life study made with anhydrous and aqueous dipropylene glycol feeds are shown in Figure 2. With anhydrous feed the activity of the catalyst was high initially, but after less than 10 kg. of the glycol had been fed, the catalyst had lost nearly all of its activity.

The run made with a feed that contained aqueous dipropylene glycol indicates that the presence of water during the first portion of the reaction period is of critical importance in extending the catalyst life. The ability to recycle recovered dipropylene glycol was demonstrated during the latter stage of the run.

Table IV. Effect of Temperature and Feed Rate in Vapor-Phase Amination of Aqueous Dipropylene Glycol

Feed/Hour, Moles

Dipropylene glycol	0.6
Water	0.6
Ammonia	3.0
Hydrogen	1.8

Run	*Space Velocity*	*Temp., ° C.*	*Conv., %*	*Yield, %*
1	460	190	78	80
2	920	190	64	80
3	460	200	75	75
4	920	200	65	78

Table V. Preparation of Pure Dimethylmorpholine Isomers

Harshaw Ni 0104 catalyst, 449 g.
Reaction temperature, 190° to 195° C.

Feed/Hour, Moles

Dipropylene glycol	0.6
Water	0.6
Ammonia	3.0
Hydrogen	1.8

Dipropylene Glycol	*Product*	*Conv., %*	*Yield, %*
1,1′-Oxydi-2-propanol	3,5-Dimethylmorpholine	78	78
2-(2-Hydroxypropoxy)-1-propanol	2,5-Dimethylmorpholine	74	74

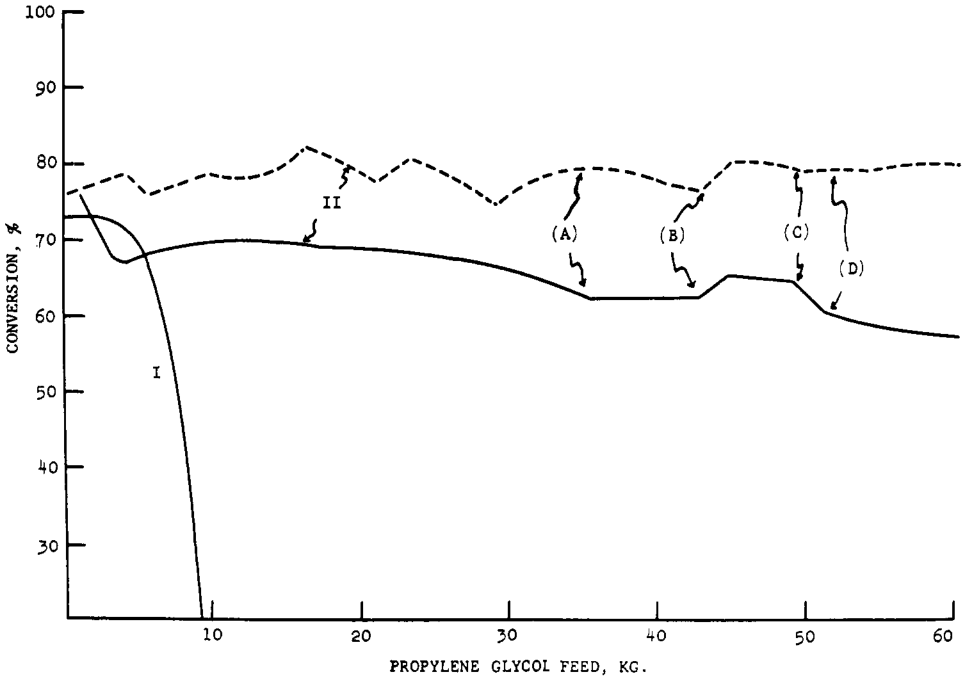


Figure 2. Catalyst life studies

—— Conversion values
– – – Yield values
A. Feed changed to dry recovered glycol
B. Feed changed to aqueous recovered glycol (1 mole H_2O/mole glycol)
C. Feed changed to fresh aqueous glycol
D. Feed changed to dry fresh glycol
I. Anhydrous dipropylene glycol
II. Aqueous (1 mole H_2O/mole dipropylene glycol)
Harshaw Ni 0104T ⅛ catalyst, 325 ml.
Reaction temperature. 190–195° C.
Feed per hour, moles

Dipropylene glycol	0.6
Ammonia	3.0
Hydrogen	1.8

The life study run was terminated at 700 hours of continuous operation. The over-all conversion of dipropylene glycol to dimethylmorpholine was 65% and the over-all yield was 79%. Even when terminated, the catalyst was still active, giving a conversion of over 60%. The production of dimethylmorpholine was 70 grams per gram of catalyst, and obviously the catalyst still had a great deal of additional production capacity.

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ALKALINE HYDROLYSIS OF SODIUM TRIMETAPHOSPHATE IN CONCENTRATED SOLUTIONS AND ITS ROLE IN BUILT DETERGENTS

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The conversion rate and mechanism of sodium trimetaphosphate to sodium tripolyphosphate in concentrated alkaline solutions were determined. For most detergent slurries, the conversion rate is fast enough so that sodium trimetaphosphate can be advantageously used as a source of sodium tripolyphosphate. Sodium trimetaphosphate seems to offer a new technology in processing built detergents.

SODIUM trimetaphosphate, $(NaPO_3)_3$ or $NaPO_3$-I, differs from other sodium meta- and/or polyphosphates in that its anion is a unique six-membered ring and it is a salt of a strong acid and a strong base (*12*). Since it does not have the desirable property of sequestering or forming soluble complexes with calcium or magnesium in a water solution (*2*), or the buffering action to maintain the desired pH of the solution, sodium trimetaphosphate heretofore has been considered as an inert salt, and for many years remained a laboratory curiosity. Therefore, sodium tripolyphosphate producers usually kept the amount of sodium trimetaphosphate in their tripolyphosphate products at a minimum. On the other hand, earlier publications (*1*, *4*) indicated that the trimetaphosphate can be hydrolyzed into sodium tripolyphosphate in a dilute alkaline solution. Whether sodium trimetaphosphate should be considered as a valuable ingredient in a phosphate builder of a synthetic detergent depends on its rate of conversion to tripolyphosphate under practical conditions.

Kinetic studies on the hydrolysis of sodium trimetaphosphate have been reported by several investigators (*3*, *5*, *6*, *7*). Their techniques, results, and conclusions differ considerably. To facilitate their studies, one or more of the following simplifications was used by these prior investigators: (1) The concentration of the test solution was very low; (2) the hydroxyl ion concentration was very high and could be assumed constant; (3) the hydroxyl ion was assumed to be only a catalyst, and the variation of hydroxyl ion concentration was neglected; (4) trimetaphosphate hydrolysis was assumed to proceed as a simple reaction—e.g., via either straight hydrolytic degradation:

$$P_3O_9^{-3} + H_2O \rightarrow H_2P_3O_{10}^{-3} \qquad (1)$$

or via alkaline hydrolysis:

$$P_3O_9^{-3} + OH^- \rightarrow HP_3O_{10}^{-4} \qquad (2)$$

or

$$P_3O_9^{-3} + 2\,OH^- \rightarrow P_3O_{10}^{-5} + H_2O \qquad (2a)$$

and/or (5) the end product was not determined but assumed to be tripoly- or acid tripolyphosphate.

Since in conventional commercial detergent processes the "solids" (nonvolatile at 110° C.) concentration in detergent slurries is very high, and the supply of the hydroxyl ion in such slurries is often limited, one could not determine from these prior data whether or not the conversion of sodium trimetaphosphate to sodium tripolyphosphate might be useful commercially in processes for the manufacture of detergents. The present study was aimed to elucidate the mechanism of the reaction of trimetaphosphate with base to yield tripolyphosphate, to measure the rate of this reaction at various "solids" concentrations and various hydroxide concentrations, and to determine the end hydrolysis (reaction) product so that the potential role of sodium trimetaphosphate in processes for manufacturing built detergents could be determined.

Experimental

The sodium trimetaphosphate used was made by heating a recrystallized monosodium orthophosphate monohydrate gradually to 610° C. and holding it at that temperature until