Tetrahedron Vol 28, pp 1965 to 1972. Pergamon Press 1972. Printed in Great Britain

REACTIONS OF TETRAKIS(DIMETHYLAMINO)ETHYLENE WITH WEAK ACIDS

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(*Received in the USA* 29 *July* 1971; *Received in the UK for publication* 27 *December* 1971)

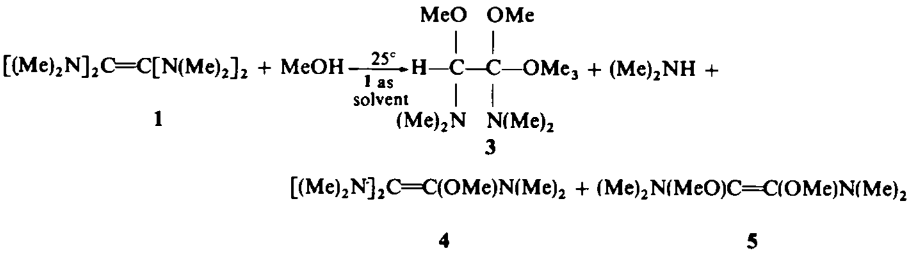
Abstract—Tetrakis(dimethylamino)ethylene reacts in methanol at 25° to give carbon–carbon bond cleavage, substitution of methoxyl for dimethylamino and addition of methanol to the double bond. The principal products are dimethylamine, dimethoxydimethylaminomethane and 1,1,2-trimethoxy-1,2-bis(dimethylamino)ethane. Minor products are methoxydimethylamino-N,N-dimethylacetamide, trimethylamine and dimethyl ether. An oxidation-reduction side reaction forms a very small amount of the radical cation of tetrakis(dimethylamino)ethylene. In the presence of sodium methoxide no carbon–carbon bond cleavage occurs and no radical cation is formed. When methanol is dissolved in tetrakis(dimethylamino)ethylene (methanol 1M), the principal products are 1,1,2-trimethoxy-1,2-bis(dimethylamino)ethane and dimethylamine with small amounts of tris(dimethylamino)methoxyethylene and 1,2-bis(dimethyl amino)-1,2-dimethoxyethylene. Tetrakis(dimethylamino)ethylene and water give dimethylamine and dimethylformamide.

TETRAKIS(DIMETHYLAMINO)ETHYLENE[1] (**1**) is an electron rich olefin that reacts with a wide variety of electrophilic reagents.* The protonated product of **1** is unstable in strong acid and an oxidation-reduction reaction occurs involving **1** and a charged species derived from **1**.[5] Trifluoroacetic acid and **1** in benzene gives octamethyloxamidinium trifluoroacetate, N,N,N',N'-tetramethyl(dimethylamino)acetamidinium trifluoroacetate and dimethylammonium trifluoroacetate.[5] Hydrochloric acid and **1** gives octamethyloxamidinium chloride, N,N-dimethylglyoxamide (hydrolysis product of **1**) and dimethylammonium chloride.[6] The corresponding reduction product was not identified.

The literature on the reaction of **1** with weak acids is contradictory and fragmentary. Pruett *et al.*[1] report that **1** reacts vigorously with alcohol and water (conditions and products not stated) while Wiberg and Buchler[6] report that the reactions of **1** with water and MeOH are sluggish even at 160°. Products were dimethylamine and dimethylformamide from **1** and water and dimethylamine and unidentified material from **1** and MeOH. In the present investigation it was found that **1** reacts with MeOH at 25° at a moderate rate, $t_{\frac{1}{2}} \sim 6$ hr (reaction 2). The reaction with water is extremely slow at 25° due in part, at least, to the mutual insolubilities of the reactants.

In contrast to the reaction of **1** with strong acids the reaction with weak acids does not involve oxidation-reduction reactions, excepting the formation of a very small amount of radical cation **17** in reactions 2 and 4. The apparent reactions are carbon–carbon bond cleavage, substitution of methoxyl for dimethylamino, addition of methanol to carbon–carbon double bond and alkylation of dimethylamine and methoxide.

* For a comprehensive discussion of the chemistry of **1** and other tetraaminoethylenes see refs 2, 3 and 4.

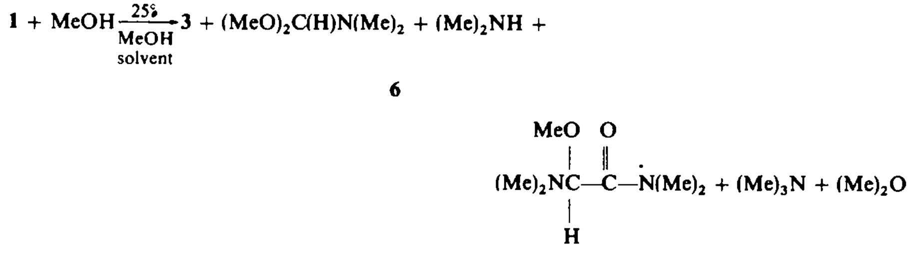


$$[(Me)_2N]_2C{=}C[N(Me)_2]_2 + MeOH \xrightarrow[\text{1 as solvent}]{25^{\circ}} H{-}\overset{\overset{MeO}{|}}{\underset{\underset{(Me)_2N}{|}}{C}}{-}\overset{\overset{OMe}{|}}{\underset{\underset{N(Me)_2}{|}}{C}}{-}OMe_3 + (Me)_2NH +$$

1 3

$$[(Me)_2N]_2C{=}C(OMe)N(Me)_2 + (Me)_2N(MeO)C{=}C(OMe)N(Me)_2 \qquad (1)$$

4 5



$$1 + MeOH \xrightarrow[\text{MeOH solvent}]{25^{\circ}} 3 + (MeO)_2C(H)N(Me)_2 + (Me)_2NH +$$

6

$$(Me)_2N\underset{\underset{H}{|}}{\overset{\overset{MeO}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}N(Me)_2 + (Me)_3N + (Me)_2O \qquad (2)$$

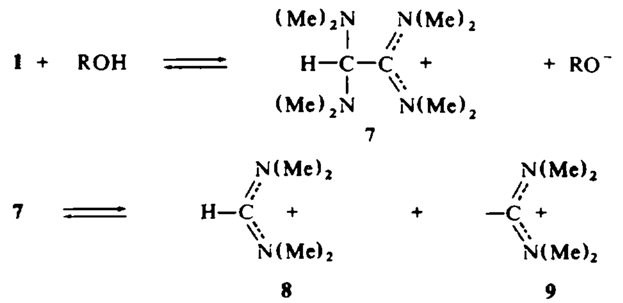
18

$$1 + MeOH \xrightarrow[\text{MeOH solvent}]{25^{\circ}\ \text{MeONa}} 3 + (Me)_2NH + 18 \qquad (3)$$

$$1 + H_2O \xrightarrow{25^{\circ}} (Me)_2NCHO + (Me)_2NH \qquad (4)$$

The reaction of **1** with MeOH was run under three different sets of conditions (reactions 1, 2 and 3). In all cases the main product (excluding dimethylamine) was 1,1,2-trimethoxy-1,2-bis(dimethylamino)ethane (**3**). In reaction 2 carbon–carbon bond cleavage, to give dimethoxydimethylaminomethane (**6**), accounted for one-third of the reaction. The addition of sodium methoxide to the MeOH solution (reaction 3) prevented carbon–carbon bond cleavage and in reaction 1, with **1** as the solvent, no carbon–carbon bond cleavage occurred either. Olefins **4** and **5** were formed in small amounts and were detected by VPC.*

A mechanism has been proposed by Lemal for the carbon–carbon bond cleavage of tetraaminoethylenes by electrophilic reagents.[7] For **1** and water or alcohol it would be:



R = Me, H

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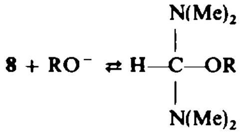
* It is possible that part or all of **5** might arise from thermal elimination of MeOH from **3** in the injector port of the VPC considering the thermal elimination of morpholine from 1,1,2,2-tetramorpholinoethane[8] and of MeOH from the MeOH adduct with 2,2-bis(3-methylbenzthiazolidine).[9]

Intermediates **8** and **9** react with the solvent to give **10**.

$$\mathbf{9} + ROH \rightleftharpoons \mathbf{8} + RO^-$$

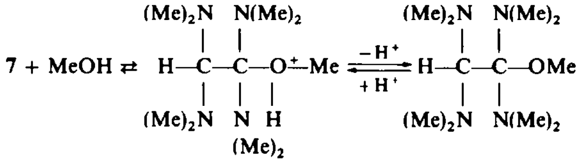


$$\mathbf{8} + RO^- \rightleftharpoons H\text{—}\overset{\displaystyle N(Me)_2}{\underset{\displaystyle N(Me)_2}{C}}\text{—}OR$$

10

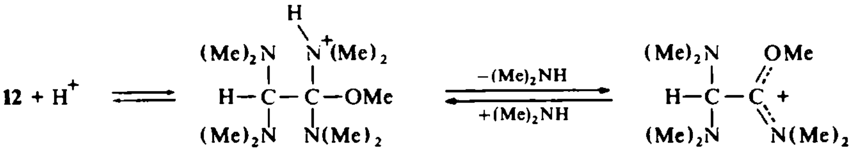
If R = H, **10** will lose dimethylamine to give DMF. If R = Me, **10** will react with another MeOH to give **6** and dimethylamine. Cleavage of the central carbon–carbon bond is the principal reaction of tetrakis(aralkylamino)ethylenes with both strong and weak acids[10,11] but was previously reported for **1** only with water at 160°.[6]

In MeOH, **1** also undergoes substitution of two dimethylamino groups by methoxyl and addition of MeOH to the double bond. A mechanism for these reactions can be written starting with intermediate **7**.



$$\mathbf{7} + MeOH \rightleftharpoons H\text{—}\overset{\displaystyle (Me)_2N}{\underset{\displaystyle (Me)_2N}{C}}\text{—}\overset{\displaystyle N(Me)_2}{\underset{\displaystyle N(Me)_2}{C}}\text{—}\underset{\displaystyle H}{\overset{+}{O}}\text{—}Me \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H\text{—}\overset{\displaystyle (Me)_2N}{\underset{\displaystyle (Me)_2N}{C}}\text{—}\overset{\displaystyle N(Me)_2}{\underset{\displaystyle N(Me)_2}{C}}\text{—}OMe$$

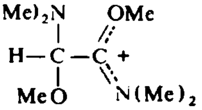
11 **12**



$$\mathbf{12} + H^+ \rightleftharpoons H\text{—}\overset{\displaystyle (Me)_2N}{\underset{\displaystyle (Me)_2N}{C}}\text{—}\overset{\displaystyle H\overset{+}{N}(Me)_2}{\underset{\displaystyle N(Me)_2}{C}}\text{—}OMe \underset{+(Me)_2NH}{\overset{-(Me)_2NH}{\rightleftharpoons}} H\text{—}\overset{\displaystyle (Me)_2N}{\underset{\displaystyle (Me)_2N}{C}}\text{—}\overset{+}{C}\genfrac{}{}{0pt}{}{\cdots OMe}{\cdots N(Me)_2}$$

13 **14**

MeOH is added to **1** to give **12** which, after protonation, loses dimethylamine to give a new ion, **14**. A dimethylamino group is replaced on the other carbon by a similar sequence to give **15**. Reaction of **15** with MeOH and deprotonation gives **3** and deprotonation of **14** and **15** gives the olefins, **4** and **5**, respectively.



$$H\text{—}\overset{\displaystyle (Me)_2N}{\underset{\displaystyle MeO}{C}}\text{—}\overset{+}{C}\genfrac{}{}{0pt}{}{\cdots OMe}{\cdots N(Me)_2}$$

15

Presumably **14** and **15** also would dissociate similarly to **7** to cleave the carbon–carbon bond. The remaining dimethylamino groups on **3** are not replaced by OMe because the required ionic intermediate would have the positive charge distributed between two OMe groups which would be much less stable than ions **7**, **14** and **15**, which have at least one dimethylamino group to accept the positive charge.

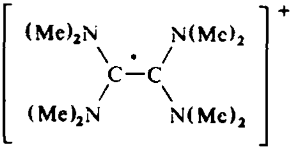
Stable addition compounds of acids to tetraaminoethylenes have never been observed and it holds here too. No evidence for **12** was found. The final product, **3**, in which two dimethylamino groups are replaced by OMe's, is isolable. In this respect, **5**, which is formally the precursor of **3**, resembles the electron rich olefins, tetramethoxyethylene[12] and 2,2-bis(3-methylbenzthiazolidine),[9] which form stable adducts with MeOH. The identification of olefins **4** and **5** marks the first time that replacement of amino groups on a tetraaminoethylene has been observed.*

These reactions are to some extent reversible since treatment of **3** with dimethylamine gives **4** and a small amount of **1**.

$$3 + (\text{Me})_2\text{NH} \longrightarrow 1 + 4 + \text{MeOH} \qquad (5)$$

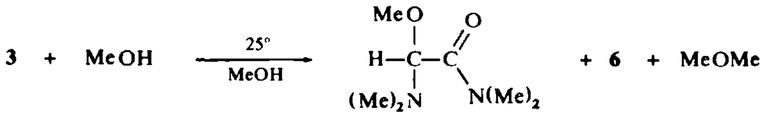
The reaction to give **3** from **1** is slowed only moderately by OMe (1 molar) (reaction 3). If the proposed mechanism is correct then the reduction in concentration of protonated species must be compensated by participation of OMe in the rate determining step such as the addition of OMe to **15** to give **3**. No carbon–carbon bond cleavage occurs, hence, dissociation of **7**, **14** and **15** must not be assisted by OMe.

A small amount of radical cation, **17**,[13] occurs in reactions 2 and 4. No oxidation-reduction products other than **17** have been detected in the MeOH reactions and **17** does not seem to be involved in the formation of **3** or **6** since increasing the concentration of **17** does not affect significantly the rate or product composition of reaction 2. The radical cation, **17**, forms when **1** is dissolved in MeOH even when extreme precautions are taken to make sure that no oxygen is in the system. Since the half-wave potentials for **1**[13] are close to the standard potential for zinc, proton reduction in MeOH is a possibility. However, a very careful search for D_2 formation from **1** in CD_3OD showed none. A small fraction of **1** may react with MeOH by the path taken with strong acids.[5,6]



17

When **3** stands in MeOH for five days, dimethylaminomethoxy-N,N-dimethylacetamide (**18**) and **6** form in 8% and 2% yield respectively.



$$3 + \text{MeOH} \xrightarrow[\text{MeOH}]{25^\circ} \text{H}-\underset{(\text{Me})_2\text{N}}{\overset{\text{MeO}}{\text{C}}}-\text{C}(=\text{O})\text{N}(\text{Me})_2 + 6 + \text{MeOMe} \qquad (6)$$

18

Dimethyl ether has been identified in the volatile fractions of this and the other reactions. When considerable dimethylamine is present, as in reaction 2, trimethyl-

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* Kliegman and Barnes[8] observed displacement of morpholino groups from 1,1,2,2-tetramorpholinoethane by MeOH to give 1,2-dimethoxy-1,2-dimorpholinoethane. The reaction could be reversed by treatment of the product with morpholine.

amine is also formed. The alkylating species may be **14** or **15**.[14] When reaction 3 was run at reflux, **18** was the only product isolated.

The structure of **3** was established on the basis of its elemental analysis and NMR spectrum. The three possible positional isomers for three OMe's and two dimethylamino groups on two carbons, in principle, are distinguishable by NMR. In the case of **3** there are six singlet peaks (Table 1); one for each OMe and dimethylamino group and one for the lone proton on carbon. The two OMe groups on one carbon give different NMR signals because they are on a carbon adjacent to an asymmetrically substituted carbon.[15]

The NMR spectrum of **4** shows four singlet peaks (Table 1). The three dimethylamino peaks, all quite close together, have δ values close to that for **1**. The mass spectrum of **4** (Table 2) shows a moderately strong parent ion at *m/e* 187 and a weak doubly charged parent ion at *m/e* 93·5. The *m/e* values at 85 and 101 are also present in the mass spectrum of **1** and represent fragments containing two amino groups attached to one carbon as occurs on one end of **4** and on both ends of **1**. Two other prominent peaks at *m/e* 72 and 88 correspond to fragments which arise from a carbon which carries an amino and an OMe.

The structure assignment of **5** is based on its mass spectrum. The parent ion at *m/e* 174 is moderately strong with M^+-15 being the strongest peak, as it was with **4**.

TABLE 1. NMR SPECTRA AT 35°[a]

Compound	Groups	δ[b]	Peak area ratios
3	$N(Me)_2$	2·38	6
(neat)	$N(Me)_2$	2·39	6
	OMe	3·10	3
	OMe	3·40	3
	OMe	3·43	3
	CH	3·77	1
4	$N(Me)_2$	2·58	6
(in benzene)	$N(Me)_2$	2·63	6
	$N(Me)_2$	2·65	6
	OMe	3·34	3
1	$N(Me)_2$	2·54	
(neat)			
18	$N(Me)_2$	2·33	6
(neat)	$N(Me)_2$	3·02, $J = 12$ Hz	6
	OMe	3·25	3
	CH	4·45	1
6	$N(Me)_2$	2·17	6
(neat)	$(OMe)_2$	3·15	6
	CH	4·18	1

[a] NMR spectra were recorded on a Varian A-60 Spectrometer.

[b] δ values are ppm with respect to TMS.

TABLE 2. MASS SPECTRAL DATA[a]

m/e	Ion	**5**	**4**	**1**
72	$CH_3\overset{+}{O}{=}C{=}NCH_3$ or $(CH_3)_2\overset{+}{N}CO$	s[b]	s	
85	$(CH_3)_2\overset{+}{N}{=}C{-}NCH_3$		s	s
88	$(CH_3)_2\overset{+}{N}C(H)OCH_3$	m	m	
93·5	M^{++}[c]		w	
101	$[(CH_3)_2N]_2\overset{+}{C}H$		m	m
159	M^+-15	s		
172	M^+-15		s	
174	M^+	m		
185	M^+-15			s
187	M^+		m	
200	M^+			s

[a] Ionizing voltage = 70 ev.
[b] w = weak, m = medium, s = strong.
[c] M = parent mass.

The absence of peaks at m/e 85 and 101 rules out a structure with two dimethylamino groups on one carbon while the peaks at m/e 72 and 88 confirm a structure with a OMe and a dimethylamino group on one carbon as in **5**.

The structure of dimethylaminomethoxy-N,N-dimethylacetamide (**18**) is based on elemental analysis, IR data (C=O at 6·02 μ) and NMR data (Table 1).

EXPERIMENTAL

Since **1** reacts so readily with oxygen all manipulations of **1** were carried out either in a N_2 atmosphrere or on the vacuum line unless otherwise stated and all reagents were carefully deoxygenated before use.

Search for D_2 *from reaction of* **1** *and* CD_3OD. One milliliter of CD_3OD, degassed five times on a vacuum line, was saturated with **1** and a sample sealed off in a glass ampoule. The ampoûle was heated for 48 hr at 50°, chilled with liquid N_2, and opened directly into a mass spectrometer. No D_2, HD, or H_2 was detected.

Reaction of **1** *and methanol with* **1** *as solvent.* One milliliter of MeOH* was made up to 25 ml with **1**. A 5 mm glass tube was loaded with some of the solution and sealed under vacuum. After 10 days (at 25°) the MeOH concentration (NMR) had decreased by 33%. (After 16 months 42% of the MeOH had reacted.) By NMR analysis **3** and dimethylamine increase in direct proportion to the amount of MeOH consumed.

In addition very small amounts of **4** and **5** were detected by VPC (20% SE-52 on Chromasorb W, column temp, 144°) in a ratio of 1 to 35. The mass spectrum† of **4** was identical with that of **4** isolated and identified in another experiment. The mass spectrum of **5** is consistent with the formula, (Table 2). Relative VPC elution times for **5**, **4** and **1** were 7, 9·5 and 12 respectively.

Reaction of 1,1,2-*trimethoxy*-1,2-*bis(dimethylamino)ethane* (**3**) *with dimethylamine.* Dimethylamine (0·15 g) and 0·15 g of **3** were combined in a 5 mm glass tube, degassed, and sealed under vacuum. After 4 days at 25° about two-thirds of **3** had reacted. After 5 months about 15% of **3** remained and after 10 months about

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* MeOH used was Matheson Coleman and Bell "anhydrous." Analysis reported on bottle indicated 0·04% water.

† Mass spectra were determined on a Hitachi Mass Spectrometer model RMU-6E. All spectra were run with an ionizing voltage of 70 ev.

5% **3** remained unreacted. As estimated from NMR data, there was 90% **4**, 5% **1**, and 5% **3**. The mass spectrum of **1** was identical with that of an authentic sample of **1**. Tris(dimethylamino)methoxyethylene (**4**) is a colorless liquid. When irradiated in a Pyrex tube under a UV lamp, there seemed to be a weak yellow fluorescence.

Treatment of **1** *with dimethylamine.* Dimethylamine (0·15 g) and 0·15 g of **1** were degassed and sealed under vacuum. After one year at 25° the NMR spectrum of the solution was unchanged. There is no detectable amount of addition product, i.e., pentakis(dimethylamino)ethane, formed.

Reaction of **1** *and methanol in methanol solution.* MeOH saturated with **1** (approximately 0·55M), was sealed in a 5 mm glass tube under vacuum. The solution assumed a bright yellow color soon after mixing. After 30 min at 25° the NMR signal for dimethylamine at $\delta = 2{\cdot}34$ was already prominent. After 3 days **1** had disappeared and the three principal products by NMR were: dimethylamine, $\delta = 2{\cdot}34$; **3** (67%), $\delta = 2{\cdot}40$, 2·44, 3·18, 3·40, 3·43, and 3·88; **6** (33%), $\delta = 2{\cdot}24$, 3·30, and 4·38. An authentic sample of **6** in MeOH gave the same NMR spectrum as reported for **6** above. The slight differences between the δ values reported above and those in Table 1 are due to solvent effects. The molar ratio of **3** to **6** was about 1 to 1. Analysis of the low boiling components by VPC (Chromasorb 103) showed dimethylamine and small amounts of dimethyl ether and Me_3N. They were identified by their VPC elution times and by their mass spectra.

Formation of radical cation of **1** *in methanol.* MeOH and **1** were separately degassed on the vacuum line by alternately freezing the sample with liquid N_2, pumping off the residual gases and melting. This cycle was repeated five times and the ultimate pressure achieved on the last freeze down-pumping state was 5×10^{-7} mm for each sample. Approximately 1 ml each of **1** and MeOH were vacuum transferred to the same receiver and thoroughly mixed. A bright yellow color developed immediately in the MeOH-rich phase. At this point any traces of oxygen still remaining in the mixture should have been eliminated because alcohols catalyze the reaction of **1** with oxygen.[3] Part of this mixture was then vacuum transferred to yet another vessel and thoroughly mixed. The MeOH-rich phase was very pale yellow initially but became more yellow in a few min and gave a strong EPR signal characteristic of the radical cation of **1**.[13]. After 24 hr the EPR signal intensity had doubled.

Reaction of **1** *and methanol with added octamethyloxamidinium chloride.* MeOH solution, 0·55 molar in **1**, and 0·010 molar in octamethyloxamidinium chloride was prepared. The rate of the reaction at 25° was followed by monitoring the change in dimethylamine concentration by NMR. The mixture was blood red from the radical cation, **17**. The half-life for the reaction was 350 min, the same as for the reaction without added octamethyloxamidinium ion. The molar ratio of **3** to **6** was also the same in both cases, 1 to 1.

Reaction of bis(dimethylamino)methoxymethane (**10**) *with methanol.* Bis(dimethylamino)methoxymethane[16] (10%) in MeOH reacts at 25° to give dimethylamine, NMR values, $\delta = 2{\cdot}33$, and **6**, $\delta = 2{\cdot}24$, 3·26, and 4·33 (ratio of 6:6:1) by the time the solution has been prepared and the sample placed in the NMR spectrometer (estimated time of 30 min). The NMR spectrum of neat *bis*(dimethylamino)methoxymethane gives peaks at $\delta = 2{\cdot}26$, 3·33, and 3·55 (ratio of 12:3:1).

Reaction of 1,1,2-*trimethoxy*-1,2-*bis*(*dimethylamino*)*ethane* (**3**) *with methanol.* A solution (20% by volume) of **3** in MeOH was sealed, under vacuum, in a 5 mm tube. In 5 days at 25°, 10% of **3** was consumed but only a minor part, about 20% of the 10% as judged by NMR analysis was **6** ($\delta = 2{\cdot}25$, 3·28, and 4·33). The other product was **18**, $\delta = 2{\cdot}35$, 3·03 ($J = 8$ Hz), 3·28, and 4·47.

Reaction of **1** *with methanol containing sodium methoxide.* MeOH, (1·09N in NaOMe) was saturated with **1**. The solution was pale yellow in contrast to the bright yellow obtained in the absence of NaOMe. The NMR peak due to **1**, $\delta = 2{\cdot}53$, was sharp in contrast to the broad peak observed in the absence of NaOMe. After 9 days at 25° no NMR signal for **1** could be detected. The main NMR peaks were due to **3** (95%), $\delta = 2{\cdot}41$, 2·46, 3·20 (3·40 under Me of MeOH), 3·45, and 3·90; and dimethylamine, $\delta = 2{\cdot}35$. Small peaks at $\delta = 3{\cdot}05$ ($J = 8$ Hz) and 3·30 are probably due to **18** (5%). There was no NMR evidence for the presence of any **6**. When the tube containing the 9 day old sample was opened to the atmosphere a transient red color developed. A rerun of the NMR spectrum after exposure to air showed no changes. The red color was probably due to a very small amount of **1** still present in the solution reacting with oxygen but insufficient to be detected by NMR.

Preparation of 1,1,2-*trimethoxy*-1,2-*bis*(*dimethylamino*)*ethane* (**3**). Twenty milliliters of **1** (0·087 mole) and 100 ml of 1·0N NaOMe in MeOH were combined and stirred for 4 days at 25° and refluxed at 280 mm pressure (about 44°) for 3 days. NMR analysis showed that **1** was gone and peaks due to **3** and **18** were present. MeOH was removed under reduced pressure until solid just appeared in the mixture. MeOH was added until the solid just disappeared. This was then extracted with 50 ml of pentane. The pentane-rich phase was separated and the pentane removed under reduced pressure and the residue distilled at 1·5 mm pressure. A fraction boiling at 42–43°/1·5 mm weighed 7·5 g. NMR analysis indicated that the material was 94% **3** and 6% **18**. This represented a 40% yield of **3**. A sample of **3** was obtained by VPC (20% SE-52 on Chromasorb W). The NMR data for 1,1,2-trimethoxy-1,2-bis(dimethylamino)ethane (**3**) are in Table 1. (Calc. for $C_9H_{22}N_2O_3$: C, 52·40; H, 10·75; N, 13·58. Found: C, 52·75; H, 10·66; N, 14·15%).

Reaction of **1** *with methanol* (1N CH_3ONa) *at reflux*. Twenty milliliters (0·087 mole) of **1** was combined with 100 ml of 1·0N NaOMe in MeOH and heated to reflux for 36 hr. The volatile material was distilled into a Dry Ice–acetone trap at 0·001 mm pressure, leaving behind the NaOMe The low boiling material was removed from the distillate by distillation at atmospheric pressure (until the pot temperature reached 100°). An attempt was made to fractionate the residue on a spinning band column but it was too high boiling. A 5 g cut (36% yield) of **18** came over at a head temperature of 50–55° at about 0·1 mm pressure. The NMR data are reported in Table 1. The IR absorption spectrum shows a strong carbonyl band at 6·02 μ. (Calc. for $C_7H_{16}N_2O_2$: C, 52·47; H, 10·07; N, 17·49. Found: C, 52·49; H, 10·14; N, 17·26%).

Reaction of **1** *with water*. Water, 1·0 g (0·055 mole) and 4·3 g (0·022 mole) of **1** were sealed in a 1·5 × 10 cm glass tube giving a two-phase system. The aqueous phase was nearly colorless and the organic phase was the characteristic pale yellow-green color of **1**. The tube was placed on a rotating wheel (4 rpm) for 1 year at 25°. At this time, visual inspection indicated little change in the colors or relative volumes of the two phases. The tube was then stored in a static condition at 25° and after 18 months the tube contained a single phase. NMR analysis indicated that the system contained dimethylamine, dimethylformamide, water, 8% of the initial amount of **1** and a small amount (2% of the DMF) of bis(dimethylamino)methane, δ 2·17 and 2·63. A synthetic mixture of dimethylformamide, dimethylamine, bis(dimethylamino)methane and water gave the same NMR spectrum as the reaction mixture, less the **1** peak. The ratio of DMF to dimethylamine was 1 to 1.

The addition of 1 ml of water to the mixture (which contained some cyclopentane as an NMR marker) caused two phases to separate again. In the lower phase there was water, dimethylamine, dimethylformamide, and cyclopentane but no **1** detectable by NMR. Hence cyclopentane is more soluble than **1** in the aqueous medium.

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