Alkylation of Alkylidenebis(dialkylamines) with Alkyl Dihalides

Charles F. Hobbs* and Harold Weingarten

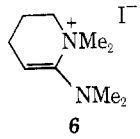
Monsanto Company, Corporate Research Department, St. Louis, Missouri 63166

Received August 30, 1973

Alkylidenebis(dialkylamines) (enediamines), **1**, undergo C-alkylation with alkyl dihalides, $X(CH_2)_nX$, to give linear diamidinium salts, **2**, and cycloalkylamidinium salts, **3**. The latter predominate when n = 2, 4, and 5. 1,3-Diiodopropane (n = 3) and **1** afforded the novel tetrahydropyridinium salt **6** by both C- and N-alkylation. Evidence for N-alkylation with other dihalides is presented. Although alkylation of the simplest bis(enediamine) **16** with methylene iodide gave the expected cyclopropanedicarboxamidinium salt **17**, bis(enediamines) **18–21** gave complex product mixtures. Formation of *N,N,N′,N′*,2-pentamethylacrylamidinium salt **14** from enediamine **10b** and *N,N,N′,N′*-tetramethylcyclopentene-1,2-dicarboxamidinium salt **22** from enediamine **21** indicates incursion of the oxidation–reduction processes in these cases.

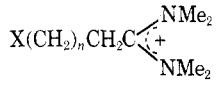
In a previous paper[1] we discussed the alkylation of alkylidenebis(dialkylamines) (enediamines) with alkyl halides. In this paper we report the extension of this work to the alkylation of enediamines and bis(enediamines) with alkyl dihalides.[2]

Our interest in this area was generated by the observation that vinylidenebis(dimethylamine) (**1**) gave an excellent yield of the glutaramidinium salt **2** (n = 1, X = I) with methylene iodide. With longer chain dihalides, however, cycloalkylation (route b, Scheme I) became predominant, giving the amidinium salts **3** and **4**, the latter being the conjugate acid of **1**. The cyclization products **3**, which were observed by nmr spectroscopy, were not isolated; rather, the reaction mixtures were hydrolyzed to obtain the cycloalkaneamides **5**. The yields of products from the two modes of reaction, a and b, are summarized in Table I.[3] In the case of 1,3-diiodopropane, none of the cyclobutane derivative (**3**, n = 3, X = I) was observed. Instead, the novel tetrahydropyridinium salt **6** was isolated in good yield.

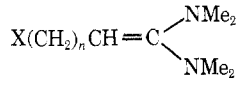


6

Presumably, the monoadducts **7** are common intermediates in all of these reactions. Displacement of halide by a second molecule of enediamine affords the linear product **2**, whereas proton abstraction by the strongly basic starting enediamine yields a new enediamine, **8**. Normally, **8**



7

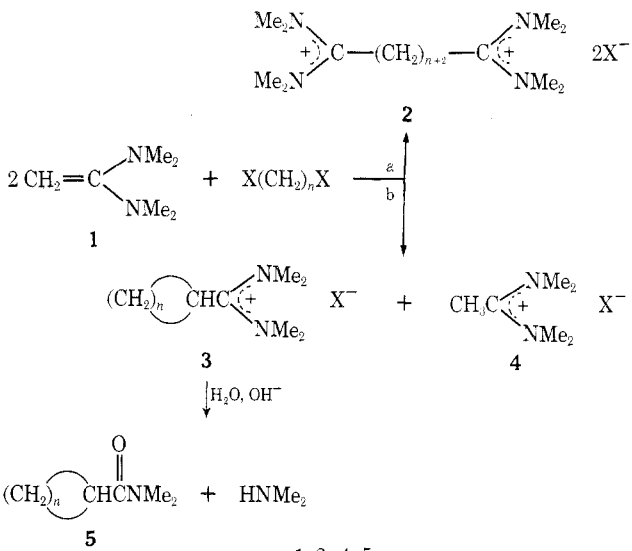


8

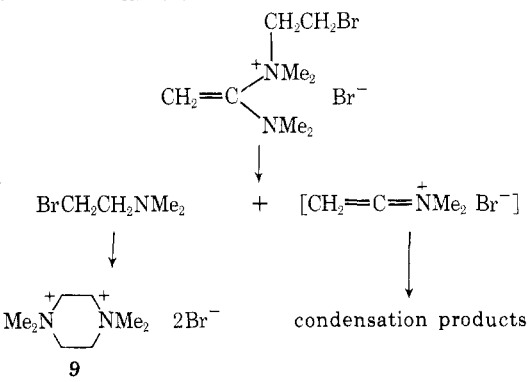
undergoes intramolecular displacement by carbon to give **3**. In the 1,3-diiodopropane case, however, **8** (n = 3) cyclizes at nitrogen rather than carbon, giving **6**. Thus, the characteristic tendency of the enediamines to alkylate at carbon with formation of the charge-stabilizing amidinium grouping[1] is overshadowed in this case by the more favorable energetics of formation of a six-membered rather than a four-membered ring.

It is likely that N-alkylation occurred to some extent with the other halides as well, although we would not expect to observe the initial products because of their instability.[1] In the case of 1,2-dibromoethane, however, we were able to isolate tetramethylpiperazinium bromide (**9**),

Scheme I



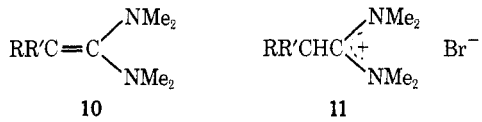
which could be formed by initial N-alkylation of the enediamine, elimination to give the ketenimmonium salt[1,4] and 2-dimethylaminoethyl bromide, and subsequent dimerization[5] of the latter.



9

Extension of the above reactions to enediamines substituted at the vinyl carbon met with only limited success. Reaction of the propenylidenediamine **10a** with 1,2-dibromoethane gave only 8% of *N,N*,1-trimethylcyclopropanecarboxamide after hydrolysis compared to 34% of the cyclopropanecarboxamide obtained from **1**. The main product was the conjugate acid, **11a**, indicating that elimination of hydrogen bromide from dibromoethane had taken place. With **10b** and 1,2-dibromoethane, only elimination to give **11b** was observed.

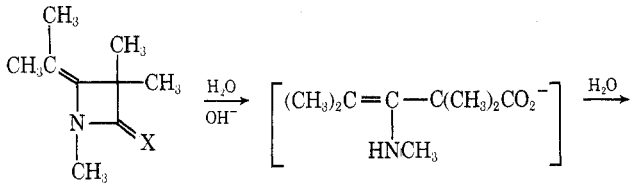
Enediamine **10b** with methylene iodide gave a complex mixture of products, two components of which were shown to be the isobutyramidinium salt **11b** and the methac-



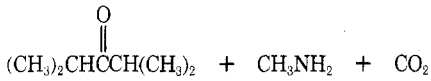
10 11

a, R = CH_3; R′ = H
b, R = R′ = CH_3

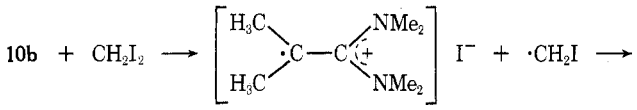
rylamidinium salt **14** by comparison of the nmr spectrum of the mixture with authentic samples.[1,6] Mild hydrolysis of the mixture yielded tetramethylammonium iodide, *N,N*-dimethylisobutyramide, *N,N*-dimethylpivalamide, *N,N*,2-trimethylacrylamide, and the β-lactam **12a.** The remainder of the product consisted of high-boiling residue. The structure of the novel β-lactam was elucidated by nmr, infrared, and mass spectral analysis, and by basic hydrolysis to methylamine and the expected diisopropyl ketones.



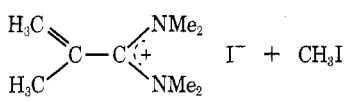
12a, X = O
b, X = NMe_2^+



The isolation of tetramethylammonium iodide and the pivalamide indicates that methylation has taken place, while the appearance of the methacrylamide suggests the incursion of an oxidation-reduction process. Both processes can be explained by oxidation of the electron-rich enediamine **10b** by methylene iodide to give radical cation **13**[6] and iodomethyl radical.



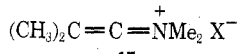
13



14

The latter abstracts hydrogen from **13** to give **14** and methyl iodide, which in turn methylates **10b** to afford the pivalamidinium salt.[1,7] Some disproportionation of radical cation **13** to **14** and isobutyramidinium salt probably also occurs.[6]

The origin of β-lactam **12a,** or its most probable precursor **12b,** is not clear although we believe that N-alkylation followed by elimination to give the ketenimmonium salt **15**[1,4] is involved. Thus, the reaction of methylene iodide



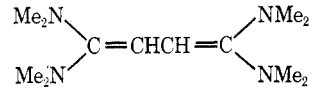
15

with ketenimmonium salt **15** (X = Cl), prepared independently,[4b] gave a mixture of salts which afforded, after hydrolysis, a low yield of lactam **12a** in addition to high-boiling residues. The mechanistic course of this reaction remains obscure.

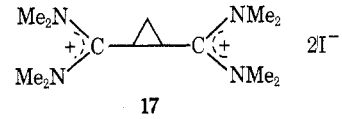
In view of the marked steric hindrance to alkylation observed in the substituted enediamines, we were surprised to find that 1,1,4,4-tetrakis(dimethylamino)-1,3-butadiene (**16**) reacted smoothly with methylene iodide to give 58% of the cyclopropane derivative **17.** Substitution of 1,2-dibromoethane for methylene iodide, however, gave a complex mixture of products in which none of the expected cyclobutane products could be detected.

Table I
Product Yields from Reaction of Vinylidenebis(dimethylamine) and Alkyl Dihalides

$X(CH_2)_nX$		Yield, %	
n	X	**2**	**5**
1	I	84	
2	Br		34
4	I	20	55
5	I	20	39



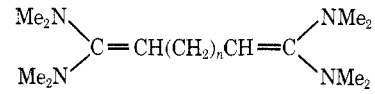
16



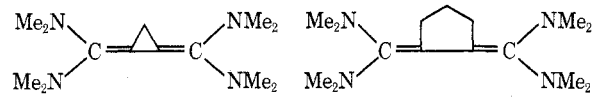
17

In contrast to **16,** the bis(enediamines) **18–20** yielded with methylene iodide or methylene bromide complex mixtures in which the major products were the conjugate acids[8] of the bis(enediamines). Tetramethylammonium ion also was detected in the reaction mixtures. Hydrolysis afforded the diamides corresponding to the starting bis(enediamines) as well as considerable high-boiling residue; we could not detect any of the expected cycloalkylated products. It is possible that the expected products were formed in small yield but did not survive under the reaction conditions.

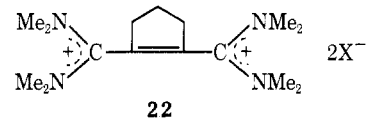
Reaction of compound **21** with methylene iodide likewise gave a complex mixture of amidinium salts.



18, *n* = 1
19, *n* = 2

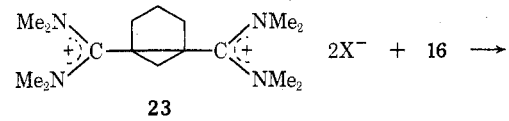


20 **21**

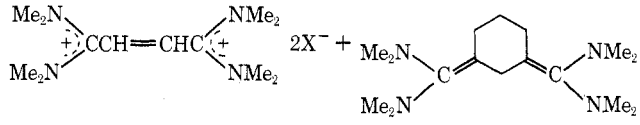


22

Hydrolysis afforded small yields of *N,N,N′,N′*-tetramethylcyclopentane-1,2-dicarboxamide and *N,N,N′,N′*-tetramethylcyclopentene-1,2-dicarboxamide, the latter being predominant. This result indicates that **21** was oxidized[6,9] to **22** (X = I) in the reaction. The oxidizing agent is not known for certain, but may be either methylene iodide, as in the case of **10b,** or the expected alkylation product **23,** as shown by an ancillary experiment. Thus, when **23** (X = PF_6)[6,9] was treated with the bis(enedi-



23



24

amine) **16**[10] in acetonitrile, nmr spectroscopy revealed the disappearance of **23** within 5–10 min and the appearance of new peaks identical with those of **24**.[6,9] This suggests that **23** may have been formed in the reaction of **21** with methylene iodide but underwent reductive ring opening[11] by **21** to yield **22** and **24**. The latter would be expected to react further with methylene iodide and hence would not be observed in this case.

Experimental Section[12]

***N,N,N′,N′*-Tetramethylcyclopropane-1,2-dicarboxamide.** Dimethyl cyclopropane-1,2-dicarboxylate[13] and dimethylamine, heated at 60° for 5 days in a pressure bottle, yielded 60% of *cis*- and *trans*-*N,N,N′,N′*-tetramethylcyclopropane-1,2-dicarboxamide, bp 123–143° (0.35 mm). Fractional crystallization afforded the pure cis isomer: mp 103–104.5°; nmr ($CDCl_3$) τ 6.86 (s) and 7.11 (s) [total 12, $(CH_3)_2NC{=}O$], 7.87 (m, 2, CHC=O), 8.5 (m, 1, ring methylene), and 8.9 (m, 1, ring methylene).

Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21; mol wt, 184. Found: C, 58.41; H, 8.63; N, 14.77; mol wt, 184.

***N,N,N′,N′*-Tetramethylcyclopentane-1,2-dicarboxamide.** Cyclopentane-1,2-dicarboxylic acid[14] was converted (94% yield) to its dimethylamide *via* the acid chloride by standard procedures. The product had bp 129–130° (11 mm), $n^{25}D$ 1.5020.

Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.20. Found: C, 62.22; H, 9.32; N, 13.40.

1,2-Bis[bis(dimethylamino)methylene]cyclopropane (20). Treatment of *N,N,N′,N′*-tetramethylcyclopropanedicarboxamide with tetrakis(dimethylamino)titanium[15] at 0° in tetrahydrofuran gave 58% of **20**: bp 98–100° (0.85 mm); $n^{25}D$ 1.5656; nmr (C_6D_6) τ 7.26 (s) and 7.32 (s) [total 24, $(CH_3)_2N$–] and 8.25 (s, 2, ring methylene). Extreme sensitivity to moisture and oxygen precluded elemental analysis.

1,2-Bis[bis(dimethylamino)methylene]cyclopentane (21). Reaction of *N,N,N′,N′*-tetramethylcyclopentane-1,2-dicarboxamide with tetrakis(dimethylamino)titanium[15] for 3 days at 90° gave 3.0 g (15%) of **21**: mp 94.5–95.0° (CH_3CN); mol wt, 266 (mass spectroscopy); nmr (C_6D_6) τ 7.36 (s, 12, $CH_3NC{=}C$), 7.60 (s, 12, $CH_3NC{=}C$), and ~8.0 (m, 6, ring protons). Extreme atmospheric sensitivity precluded elemental analysis.

Vinylidenebis(dimethylamine) with Methylene Iodide. A solution of 2.28 g (0.02 mol) of vinylidenebis(dimethylamine) (**1**),[15] 2.68 g (0.01 mol) of methylene iodide, and 4 ml of dry acetonitrile was allowed to stand at room temperature for 40 hr. The solid product was collected by filtration and recrystallized from acetonitrile to obtain 4.2 g (84%) of *N,N,N′,N′,N″,N″,N‴,N‴*-octamethylglutaramidinium diiodide (**2**, n = 1, X = I), mp 233–234°.

Anal. Calcd for $C_{13}H_{30}I_2N_4$: C, 31.47; H, 6.09; I, 51.15; N, 11.29. Found: C, 31.14; H, 5.94; I, 51.31; N, 11.01.

The bis(tetraphenylborate) salt had mp 250–252°; nmr (CD_3CN) τ ~2.9 (m, 40, phenyl), 7.03 (s, 24, $^+NCH_3$), 7.4 (m, 6, $-CH_2-$).

Vinylidenebis(dimethylamine) with 1,2-Dibromoethane. A mixture of 11.4 g (0.1 mol) of **1**, 9.4 g (0.05 mol) of 1,2-dibromoethane, and 60 ml of dry acetonitrile was heated to 70° for 24 hr. The mixture then was cooled and filtered to remove crystalline precipitate. The crystalline product, 0.1 g (1.3%), was recrystallized from aqueous ethanol to give *N,N,N′,N′*-tetramethyl-1,4-piperazinium dibromide (**9**): mp 355° dec; nmr (CF_3CO_2H) τ 5.78 (s, 8, CH_2N^+), 6.37 (s, 12, CH_3N^+). The nmr spectrum was identical with that of an authentic sample;[16] the mixture melting point was 356° dec.

The original filtrate was freed of solvent at the rotary evaporator and the resulting solid was hydrolyzed in the cold with 100 ml of 2 *N* sodium hydroxide solution. Extraction with ether, followed by distillation of the extract, afforded a mixture of *N,N*-dimethylacetamide and *N,N*-dimethylcyclopropanecarboxamide, mole ratio 2.3:1. Redistillation afforded 1.9 g (34%) of *N,N*-dimethylcyclopropanecarboxamide: bp 75–78° (10 mm); $n^{25}D$ 1.4673; nmr (CCl_4) τ 6.8 (s, broad, 6, $OCNCH_3$), ~8.15 (m, 1, CHCO), ~9.25 (m, 4, ring protons). The product was identical (ir, nmr, and vpc) with an authentic sample prepared from cyclopropanecarboxylic acid chloride and dimethylamine.

Only 13% of the cyclopropanecarboxamide was obtained when dimethylformamide was substituted for acetonitrile as solvent.

Vinylidenebis(dimethylamine) with 1,3-Diiodopropane. A solution of 11.4 g (0.10 mol) of **1**, 14.8 g (0.05 mol) of 1,3-diiodopropane, and 20 ml of dry acetonitrile was allowed to stand at room temperature for 3 days. The solution was concentrated in an inert atmosphere and then filtered to obtain 8.9 g (63%) of 6-dimethylamino-1,1-dimethyl-1,2,3,4-tetrahydropyridinium iodide (**6**): mp 195–196° dec; nmr (CD_3CN) τ 4.04 (m, 1, HC=C), 6.13 (m, 2, CH_2N^+), 6.71 (s, 6, CH_3N^+), 7.36 (s, 6, CH_3N), and 7.8 (m, 4, CCH_2CH_2C). Addition of trifluoroacetic acid caused the disappearance of peaks at τ 4.04 and 7.36 and the appearance of two new singlets at τ 5.92 and 6.04, ratio 1:1 [$=N(CH_3)_2^+$].

Anal. Calcd for $C_9H_{19}IN_2$: C, 38.31; H, 6.79; N, 9.93. Found: C, 38.45; H, 6.80; N, 9.98.

Compound **6** was dissolved in excess dilute hydrochloric acid and allowed to stand for 5 days. The solution was basified with 50% sodium hydroxide in the cold and continuously extracted with ether. Distillation of the ether extract afforded 4.7 g (55%) of 5-dimethylamino-*N,N*-dimethylpentanamide: bp 68° (0.25 mm) [lit.[17] bp 107–108° (2 mm)]; $n^{25}D$ 1.4601; nmr (C_6D_6) τ 7.25 (s) and 7.32 (s) [6 total, $OCN(CH_3)_2$], 7.91 [s + m, 10, $(CH_3)_2N$, CH_2N, and CH_2CO], and 8.4 (m, 4, CCH_2CH_2C).

Anal. Calcd for $C_9H_{20}N_2O$: C, 62.75; H, 11.70; N, 16.26; mol wt, 172. Found: C, 62.65; H, 11.76; N, 16.40; mol wt, 172.

Vinylidenebis(dimethylamine) with 1,4-Diiodobutane. A solution of 9.12 g (0.08 mol) of **1**, 12.4 g (0.04 mol) of 1,4-diiodobutane, and 20 ml of dry acetonitrile was allowed to stand for 4 days. The mixture was filtered to remove 4.4 g (20%) of crystals, a small sample of which was recrystallized from acetonitrile to give *N,N,N′,N′,N″,N″,N‴,N‴*-octamethyloctanediamidinium diiodide (**2**, n = 4, X = I): mp 265–267°; nmr (CF_3CO_2H) τ 6.70 (s, 24, $^+NCH_3$), 7.2 (m, 4, $^+CCH_2$), and 7.70 (m, 8, CCH_2CH_2C).

Anal. Calcd for $C_{16}H_{36}I_2N_4$: C, 35.70; H, 6.74; I, 47.15; N, 10.41. Found: C, 35.77; H, 6.76; I, 47.11; N, 10.34.

The filtrate and the remainder of the crystals were recombined and treated with 60 ml of 2 *N* sodium hydroxide solution. The aqueous solution was continuously extracted with ether and the ether extract was distilled to obtain 3.1 g (55%) of *N,N*-dimethylcyclopentanecarboxamide: bp 94–95° (7 mm); $n^{25}D$ 1.4765 [lit.[18] bp 64° (0.5 mm); $n^{25}D$ 1.4759]; nmr (CCl_4) τ 6.97 (s), 7.14 (s) and ~7.1 (m) (7 total, $O{=}CNCH_3$ and CHC=O), and ~8.34 (m, 8, ring protons).

Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92; mol wt, 141. Found: C, 67.92; H, 10.76; N, 10.07; mol wt, 141.

The pot residue from the above distillation was recrystallized from tetrahydrofuran to obtain 0.5 g (5%) of *N,N,N′,N′*-tetramethylsuberamide: mp 86–87°; nmr (CCl_4) τ 7.01 (s) and 7.11 (s) [12 total, $O{=}CN(CH_3)_2$], 7.78 (t, 4, $O{=}CCH_2$), and 8.48 (m, 8, CCH_2C).

Anal. Calcd for $C_{12}H_{24}N_2O_2$: C, 63.12; H, 10.59; N, 12.27; mol wt, 228. Found: C, 62.88; H, 10.48; N, 12.02; mol wt, 228.

Vinylidenebis(dimethylamine) with 1,5-Diiodopentane. A solution of 11.4 g (0.1 mol) of **1** and 16.2 g (0.05 mol) of 1,5-diiodopentane in 20 ml of acetonitrile was kept at room temperature for 2 days. The reaction mixture was cooled in ice and then filtered to obtain 5.6 g (20%) of crude *N,N,N′,N′,N″,N″,N‴,N‴*-octamethylnonanediamidinium diiodide (**2**, n = 5, X = I): analytical sample mp 171.5–172°; nmr (CD_3CN) τ 6.78 (s, 24, $^+NCH_3$), 7.26 (m, 4, $^+CCH_2$), and 8.54 [m, 10, $C(CH_2)_5C$].

Anal. Calcd for $C_{17}H_{38}I_2N_4$: C, 36.97; H, 6.93; I, 45.95; N, 10.14. Found: C, 37.38; H, 6.81; I, 45.85; N, 10.06.

The filtrate and crystals, except for the analytical sample, were recombined and hydrolyzed with 75 ml of 2 *N* sodium hydroxide to obtain 3.0 g (39%) of *N,N*-dimethylcyclohexanecarboxamide and 1.7 g (14%) of *N,N,N′,N′*-tetramethylnonanedicarboxamide.

N,N-Dimethylcyclohexanecarboxamide exhibited the following properties: bp 107–108° (7 mm) [lit.[19] bp 158° (44 mm)]; nmr (C_6H_6) τ 7.30 (s, broad, 6, OCNCH), 7.7 (m, 1, HCCO), and 8.5 (m, 10, ring protons).

Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02; mol wt, 155. Found: C, 69.62; H, 11.42; N, 9.11; mol wt, 155.

N,N,N′,N′-Tetramethylnonanedicarboxamide had bp 175–177° (0.3 mm); mp 36–37° [lit.[20] mp 40–41°]; nmr (C_6H_6) τ 7.25 and 7.46 (singlets, 12 total, $OCNCH_3$), 7.96 (m, 4, $OCCH_2$), and 8.5 [m, 10, $C(CH_2)_5C$].

Anal. Calcd for $C_{13}H_{26}N_2O_2$: C, 64.42; H, 10.81; N, 11.56; mol wt, 242. Found: C, 64.54; H, 10.75; N, 11.56; mol wt, 242.

Propenylidenebis(dimethylamine) (10a) with 1,2-Dibromoethane. A solution of 12.8 g (0.10 mol) of **10a**[15] and 9.4 g (0.05 mol) of 1,2-dibromoethane in 40 ml of dry acetonitrile was heated at 70° for 5 days. The acetonitrile was removed at the rotary evaporator and the residue was treated with 75 ml of 2 *N* sodium hydroxide. The aqueous solution was continuously extracted with ether and the ether extract was distilled to obtain, after a large forerun of *N,N*-dimethylpropanamide, 0.5 g (8%) of

crude *N,N*,1-trimethylcyclopropanecarboxamide: bp 105° (13 mm); nmr (C_6H_6) τ 7.19 [s, 6, O=CN(CH_3)$_2$], 8.84 (s, 3, CCH_3), 9.15 (m, 2, ring protons), and 9.58 (m, 2, ring protons); mass spectrum (70 eV) *m/e* 127, 112, 83, 72, 55, 44. A satisfactory element analysis was not obtained.

2-Methylpropenylidenebis(dimethylamine) (10b) with Methylene Iodide. A solution of 13.4 g (0.05 mol) of methylene iodide and 14.2 g (0.10 mol) of **10b**[15] in 25 ml of dry acetonitrile was heated at reflux for 7 days. *N,N,N',N'*,2-Pentamethylpropionamidinium iodide (**11b**) and *N,N,N',N'*,2-pentamethylacrylamidinium iodide (**14**) were identified in the mixture by comparison of the nmr spectra with those of authentic samples.[1,6] The mixture was filtered to obtain 9.7 g (0.048 mol) of crude tetramethylammonium iodide. The tetraphenylborate had mp 370–375°; nmr (acetone-d_6) τ 2.80 (m, 20, phenyl) and 6.67 (s, 12, CH_3N^+).

Anal. Calcd for $C_{28}N_{32}BN$: C, 85.47; H, 8.21; N, 3.56. Found: C, 85.55; H, 8.23; N, 3.66.

The filtrate from above was stripped of solvent at reduced pressure and the residue was treated with cold 2 *N* sodium hydroxide. The hydrolysis mixture was extracted with ether and the extract was distilled to obtain, besides 8 g of tar, 1.7 g of a 4:1:1 mixture of *N,N*-dimethylisobutyramide, *N,N*-dimethylpivalamide (identified by vpc and mass spectroscopy), and *N,N*,2-trimethylacrylamide, respectively. The latter was identified by comparison of vpc retention times and nmr spectrum with those of an authentic sample prepared by hydrolysis of the corresponding amidinium salt:[6] nmr (CCl_4) τ 4.84 (m, 1, HC=C), 5.03 (m, 1, HC=C), 7.02 (s, 6, O=CNMe_2), and 8.09 (m, 3, CH_3C=).

In addition, 0.8 g (10%) of the β-lactam, 4-isopropylidene-*N*,3,3-trimethyl-2-azetidinone (**12a**), was obtained: bp 100–105° (17–20 mm); nmr (CCl_4) τ 6.96 (s, 3, CH_3NC=O), 8.23 (s, 3, CH_3C=C), 8.39 (s, 3, CH_3C=C), and 8.73 [s, 6, $(CH_3)_2C$]; mass spectrum (70 eV) *m/e* (rel intensity) 153 (1), 152 (3), 96 (10), 83 (12), 82 (10), 81 (37), 69 (4), 68 (11), 67 (4), 56 (6), 55 (6), 54 (4), 53 (7), 42 (45), 41 (37), 28 (100); ir (CCl_4) 1704 and 1790 (C=O) and 1645 cm^{-1} (>C=C<). A satisfactory element analysis could not be obtained.

Hydrolysis of the lactam, carried out in alcoholic sodium hydroxide overnight at 80°, afforded methylamine, identified by its nmr spectra, and diisopropyl ketone, identified by comparison of vpc retention times and nmr spectrum with those of an authentic sample.

1-Chloro-*N,N*,2-trimethylpropenylamine (15) with Methylene Iodide. A mixture of 20 g (0.15 mol) of 1-chloro-*N,N*,2-trimethylpropenylamine,[4] 20 g (0.075 mol) of methylene iodide, and 20 ml of dry acetonitrile was heated for 72 hr at 70° under a nitrogen atmosphere. The bulk of the acetonitrile was removed by distillation under reduced pressure, the dark red residue was taken up in water, and the solution was extracted with ether. Distillation of the ether extract afforded 4.8 g of recovered methylene iodide. The water solution was made basic with 6 *N* sodium hydroxide and extracted with ether, and the extract was distilled to obtain 0.8 g of β-lactam **12a**, shown by vpc and infrared and nmr spectroscopy to be identical with that obtained from the reaction of **10b** and methylene iodide. The remainder of the product consisted of high-boiling residue which could not be identified.

1,1,4,4-Tetrakis(dimethylamino)butadiene (16) with Methylene Iodide. A solution of 11.3 g (0.05 mol) of **16**[15] in 10 ml of dry acetonitrile and a solution of 13.4 g (0.05 mol) of methylene iodide in 10 ml of dry acetonitrile were added simultaneously in a dropwise manner at room temperature to 20 ml of acetonitrile over a period of 18 hr. The mixture was allowed to stand for 2 days, then was concentrated to one-half the original volume and filtered to obtain 14.34 g (58%) of *trans-N,N,N',N',N'',N'',N''',N'''*-octamethyl-1,2-cyclopropanedicarboxamidinium diiodide (**17**): analytical sample mp 252–254° dec; nmr (CF_3CO_2H) τ 6.60 [s, 24, $^+N(CH_3)_2$], 7.11 (m, 2, $^+$CCH), and 7.84 (m, 2, cyclopropane methylene).

Anal. Calcd for $C_{13}H_{28}I_2N_4$: C, 31.59; H, 5.71; I, 51.36; N, 11.34. Found: C, 31.77; H, 5.83; I, 51.16; N, 11.35.

The crystals were recombined with the filtrate and the entire reaction mixture was hydrolyzed with 60 ml of 2 *N* sodium hydroxide. The aqueous solution was continuously extracted with ether, and the ether extract was distilled to obtain 3.7 g (40%) of *trans-N,N,N',N'*-tetramethyl-1,2-cyclopropanedicarboxamide: bp 110–111° (0.3 mm); mp 57–60° (lit.[21] mp 56–58°); nmr (CCl_4) τ 6.80 and 7.10 [singlets, 12 total, OCN(CH_3)$_2$], 7.78 (m, 2, OCCH), and 8.83 (m, 2, cyclopropane methylene).

Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21; mol wt, 184. Found: C, 58.50; H, 8.69; N, 15.19; mol wt, 184.

1,2-Bis[bis(dimethylamino)methylene]cyclopentane (21) with Methylene Iodide. A solution of 3.11 g (0.013 mol) of **21**[6] and 3.40 g (0.013 mol) of methylene iodide in 50 ml of acetonitrile was allowed to stand at room temperature for 10 days. The acetonitrile was evaporated under vacuum and the residue was treated with 2 *N* sodium hydroxide. The mixture was continuously extracted with ether and the ether extract was distilled to obtain 0.6 g of material, bp 110–115° (0.15 mm), consisting of 72% of *N,N,N',N'*-tetramethylcyclopent-1-ene-1,2-dicarboxamide and 20% of *N,N,N',N'*-tetramethylcyclopentane-1,2-dicarboxamide. The two amides were separated by preparative vpc and the former was identified by comparison of its mass spectrum, vpc retention time, and nmr spectrum with those of an authentic sample prepared by silver nitrate oxidation[6,9] of **21** to *N,N,N',N',N'',N'',N''',N'''*-octamethylcyclopent-1-ene-1,2-dicarboxamidinium iodide **22**, X = I) followed by basic hydrolysis: nmr (C_6D_6) τ 7.34 [s, 12, O=CN(CH_3)$_2$], 7.49 (2 d, 4, J = 7 and ~1 Hz, CH_2CH_2C=C), and 8.32 (2 t, 2, J = 7 and ~1 Hz, $CH_2CH_2CH_2$); mass spectrum (70 eV) *m/e* 210, 182, 167.

Acknowledgment. We thank Mrs. J. S. Wager and Mr. D. E. McMackins for certain preparations.

Registry No.—**1**, 815-62-3; **2** (*n* = 1, X = I), 50483-83-5; **2** (*n* = 1, X = Ph_4B), 50477-43-5; **2** (*n* = 4, X = I), 50483-84-6; **2** (*n* = 5, X = I), 50483-85-7; **6**, 50483-86-8; **9**, 24996-75-6; **10a**, 815-67-8; **10b**, 10596-50-6; **11b**, 16487-61-9; **12a**, 50483-91-5; **14**, 50483-92-6; **15**, 26189-60-6; **16**, 10596-53-9; **17**, 50486-74-3; **20**, 50483-95-9; **21**, 50483-96-0; *cis-N,N,N',N'*-tetramethylcyclopropane-1,2-dicarboxamide, 50486-75-4; *trans-N,N,N',N'*-tetramethylcyclopropane-1,2-dicarboxamide, 22299-29-2; dimethyl cyclopropane-1,2-dicarboxylate, 702-28-3; *N,N,N',N'*-tetramethylcyclopentane-1,2-dicarboxamide, 50483-98-2; cyclopentane-1,2-dicarboxylic acid, 50483-99-3; methylene iodide, 75-11-6; 1,2-dibromoethane, 106-93-4; *N,N*-dimethylcyclopropanecarboxamide, 17696-23-0; 1,3-diiodopropane, 627-31-6; 5-dimethylamino-*N,N*-dimethylpentanamide, 22041-47-0; 1,4-diiodobutane, 628-21-7; *N,N*-dimethylcyclopentanecarboxamide, 50484-00-9; *N,N,N',N'*-tetramethylsuberamide, 3644-93-7; 1,5-diiodopentane, 628-77-3; *N,N*-dimethylcyclohexanecarboxamide, 17566-51-7; *N,N,N',N'*-tetramethylnonanedicarboxamide, 13424-87-8; *N,N*,1-trimethylcyclopropanecarboxamide, 50484-04-3; tetramethylammonium tetraphenylborate, 15525-13-0; *N,N*,2-trimethylacrylamide, 6976-91-6; *N,N,N',N'*-tetramethylcyclopent-1-ene-1,2-dicarboxamide, 50484-06-5.

References and Notes

(1) C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, **33**, 2385 (1968).
(2) Reported in part by C. F. Hobbs and H. Weingarten, *J. Amer. Chem. Soc.*, **91**, 780 (1969).
(3) The main course of reaction between **1** and 1,2-dibromoethane was elimination by the strongly basic enediamine to yield vinyl bromide and **4**.
(4) H. Weingarten, *J. Org. Chem*, **35**, 3970 (1970); (b) J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2869, 2870 (1972).
(5) L. Knorr, *Ber.*, **37**, 3507 (1904).
(6) H. Weingarten and J. S. Wager, *J. Org. Chem.*, **35**, 1750 (1970).
(7) A careful check of the methylene iodide showed no detectable methyl iodide, eliminating it as a source of the methylation observed.
(8) The conjugate acids were identified in the mixture by comparison of the nmr spectra with those of authentic samples prepared by addition of trifluoroacetic acid to acetonitrile solutions of the bis (enediamines).
(9) H. Weingarten and J. S. Wager, *Tetrahedron Lett.*, 3267 (1969).
(10) Compound **16** rather than **21** was used in order to simplify the nmr analysis; the results should be analogous.
(11) This is the reverse of oxidative coupling of **24** to give **23**.[6,9]
(12) Melting points are corrected; boiling points are uncorrected. Molecular weights were determined by mass spectroscopy. All reactions, manipulations, and distillations involving enediamines were performed in an atmosphere of dry nitrogen.
(13) L. L. McCoy, *J. Amer. Chem. Soc.*, **80**, 6558 (1958).
(14) E. J. Eisenbraun, P. G. Hanel, K. S. Schorno, Sr. St. Francis Dilgen, and J. Osiecki, *J. Org. Chem.*, **32**, 3010 (1967).
(15) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).
(16) F. G. Mann and F. C. Baker, *J. Chem. Soc.*, 1881 (1957).
(17) V. M. Solov'ev and A. P. Skoldinov, *Zh. Obshch. Khim.*, **33**, 1821 (1963); *Chem. Abstr.*, **59**, 7360e (1963).
(18) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *J. Amer. Chem. Soc.*, **79**, 4729 (1957).
(19) H. E. Baumgarten, F. A. Bower, and T. T. Okamota, *J. Amer. Chem. Soc.*, **79**, 3145 (1957).
(20) V. P. Kuceski, U. S. Patent 3,288,794 (Nov 29, 1966).
(21) A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, **81**, 2012 (1959).