

## A SYNTHESIS AND PROPERTIES OF 1-SUBSTITUTED 1,4,5,6-TETRAHYDROPYRIMIDINES

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**Abstract**-The condensation of 1-substituted 1,3-diaminopropane with *N,N*-dimethylformamide dimethylacetal gives 1-alkyl- or aryl-1,4,5,6-tetrahydropyrimidines (**2**) and (**3**). Alkylation of the tetrahydropyrimidine derivatives with alkyl halides produces the 1,3-dialkyltetrahydropyrimidinium salts (**4** and **5**). The attempted dehydrogenation of **2** with sulfur leads to insertion of sulfur on the molecule.

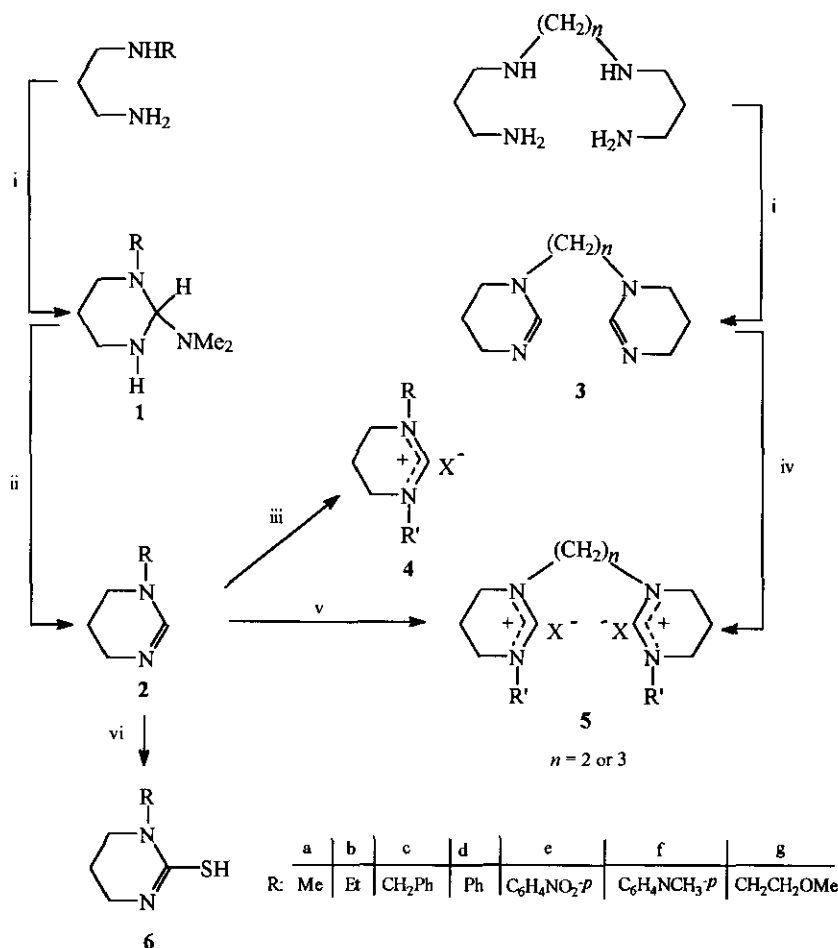
### INTRODUCTION

Recently much interest has been focused on the chemistry of 1,4,5,6-tetrahydropyrimidine derivatives. When properly substituted they can act as neuromuscular blocking,<sup>1</sup> cardiovascular<sup>2</sup> and antidepressant<sup>3</sup> agents. Bronchodilator and antihistaminic activity has been claimed for 1-(2-phenylethyl)-2-benzyl-1,4,5,6-tetrahydropyrimidine.<sup>4</sup> Fatty tetrahydropyrimidines are widely used as surface-active compounds such as emulsifiers and adhesive agents.<sup>5</sup> In addition a variety of reactive tetraaminoalkenes containing pyrimidine skeleton may be prepared *via* intermediacy of the tetrahydropyrimidinium salts.<sup>6</sup> The latter compounds are readily available from the reactions of 1-alkyl-1,4,5,6-tetrahydropyrimidines with alkyl halides (for details see below). The 1,4,5,6-tetrahydropyrimidine system is generally prepared *via* the condensation of 1,3-diaminopropanes with carboxylic acids or derivatives at high temperatures. For the cyclization reaction of 1,3-diaminopropanes to form tetrahydropyrimidines, 2,2-dimethylpropionic acid,<sup>7</sup> esters,<sup>8</sup> trialkyl orthoesters,<sup>9</sup> *N,N*-biscarbomethoxy-*S*-methylisothiourea,<sup>10</sup> 2-methyl-2-thiopseudourea,<sup>3</sup> *S,S*-dimethyl-*N*-tosyliminodithiocarbonimidate<sup>11</sup> and acetamide salts<sup>12</sup> could be used. The 1- or 1,3-disubstituted tetrahydropyrimidines are also available by the action of polyphosphoric acid<sup>13</sup> or phenyl phosphorodiamidate<sup>14</sup> on the corresponding *N*-substituted trimethylenediamines. We now report a synthesis *via* *N,N*-dimethylformamide dimethylacetal<sup>15</sup> as an alternative to the above.

### RESULTS and DISCUSSION

The observation that commercially available *N,N*-dimethylformamide dimethylacetal reacts with 1- substituted and 1,2-disubstituted ethylenediamines to give high yields of 2-imidazolines<sup>16</sup> and tetraaminoalkenes,<sup>17</sup> respectively, prompted us to examine the possible general usefulness of this reagent<sup>15</sup> for the generation of 1,4,5,6-tetrahydropyrimidines. Cyclization was performed by refluxing the mixture of 1,3-diamines with about 10% excess of the acetal.

The reaction of the acetal with 1,3-diaminopropanes proceeds *via* 2-dimethylaminohexahydropyrimidines (**1**); in cases where R = aryl, the intermediate (**1**) was isolated and upon further heating **1** was converted into **2** by elimination of dimethylamine (Scheme 1).



**Scheme 1 Reagents and conditions:** i, Me<sub>2</sub>NCH(OMe)<sub>2</sub>, 90°C; ii, 190-200°C; iii, THF, R'-X, 20°C; iv, DMF, R'-X; v, DMF, X-(CH<sub>2</sub>)<sub>n</sub>-X (n = 2 or 3), 20°C; vi, toluene, S<sub>8</sub>, 200 psi pressure, 180°C.

We have extended the reaction of the acetal to the tetraamines such as *N,N'*-bis(3-aminopropyl)ethylenediamine or *N,N'*-bis(3-aminopropyl)-1,3-propanediamine and found that at *ca.* 100°C in toluene for 3 h 80% yield of **3** (n = 2 or 3) could be obtained.

The physical and spectroscopic properties of the 1,4,5,6-tetrahydropyrimidines are recorded in Tables 1-3. Some of the pyrimidines are hygroscopic, therefore their elemental analysis data are missing in Table 1. The <sup>1</sup>H and <sup>13</sup>C nmr spectra were consistent with the proposed structures. The proton at C-2 is highly acidic (δ = 7 - 8 ppm).

As expected, the tetrahydropyrimidines (**2**) and (**3**) are good nucleophiles. Thus, they were alkylated cleanly at N-3 with a slight excess of alkyl halide in THF or DMF to give the quaternary salts (**4**) and (**5**), respectively. The bridged

Table I Yields, bp (mp) data for compound (1, 2, 3, 4 and 5).

Compound No	n	Y	R	R'	X	Yield (%)	mp (°C)	bp (°C/1mmHg)	ν (C=N)	Found (calculated) (%)		
										C	H	N
1d	-	NMe <sub>2</sub>	Ph			71		101-102				
1e	-	NMe <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>			85	70-71	-				
1f	-	OMe	C <sub>6</sub> H <sub>4</sub> Me- <i>p</i>			85		110-112				
2a	-	-	Me			95		178-180/760				
2c	-	-	CH <sub>2</sub> Ph			90	61-62	169-170				
2d	-	-	Ph			91		124-125				
2e	-	-	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>			80	144-145	-				
2f	-	-	C <sub>6</sub> H <sub>4</sub> Me- <i>p</i>			72		157-158				
2g	-	-	CH <sub>2</sub> CH <sub>2</sub> OMe			82		57-58				
3	2	-	-			78		173-174				
3'	3	-	-			87		177-178				
4a	-	-	Me	Me	I	85	79-80	-	1702	29.6 (30.02)	5.0 (5.46)	11.1 (11.67)
4c			CH <sub>2</sub> Ph	Me	I	73	118-119	-	1702	45.10 (45.58)	5.80 (5.42)	9.0 (8.86)
4d			Ph	Me	I	61	159-160	-	1702	43.1 (43.71)	4.5 (4.97)	8.9 (9.27)
4e			C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	Me	I	60	180-182	-	1702	37.8 (38.04)	3.9 (4.07)	11.9 (12.11)
4f			C <sub>6</sub> H <sub>4</sub> Me- <i>p</i>	Me	I	65	157-158	-	1702	45.1 (45.56)	5.3 (5.42)	8.9 (8.86)
4h			Me	Et	I	83	66-67	-	1702	32.8 (33.07)	5.8 (5.95)	10.9 (11.02)
4i			CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	Cl	82	222-223 <sup>a</sup>	-	1702	67.8 (67.25) <sup>b</sup>	7.2 (7.49)	8.8 (8.61)
5a	2	-	-	Me	I	81 <sup>c</sup>	241-242 <sup>a</sup>	-	1677	30.9 (30.12)	5.4 (5.06)	11.4 (11.72)
5b	2	-	-	Et	I	90 <sup>c</sup>	252-253 <sup>a</sup>	-	1699	33.7 (33.20)	5.9 (5.58)	10.8 (11.07)
5a'	3	-	-	Me	I	93 <sup>c</sup>	119-120	-	1690	31.3 (31.71)	5.7 (5.33)	11.2 (11.38)
5b'	3	-	-	Et	I	88 <sup>c</sup>	110-111	-	1684	34.3 (34.61)	6.1 (5.81)	11.0 (10.77)
5c'	3	-	-	CH <sub>2</sub> Ph	Cl	75 <sup>c</sup>	71-72	-	1685	65.5 (65.04)	7.3 (7.42)	12.4 (12.18)

<sup>a</sup> Decomposes. <sup>b</sup> 1 mol water required, <sup>c</sup> Route iv (Scheme 1)

Table 2 <sup>1</sup>H Nmr spectroscopic data with assignments for 1, 2, 3, 4 and 5.<sup>†</sup>

Compound No	2 -	4,6 -	5 -	Others
1d	7.2 (s)	3.3 (m)	1.9 (m)	7.0 (m) C <sub>6</sub> H <sub>5</sub> ; 2.8 (s) N(CH <sub>3</sub> ) <sub>2</sub>
1e	7.2 (s)	3.3 (m)	1.8 (t, J 5)	6.5 (2 H, d, J 9.0) and 8.0 (2 H, d, J 9.1) C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ; 2.9 (s) N(CH <sub>3</sub> ) <sub>2</sub>
1f	7.2 (s)	3.4 (m)	1.8 (t, J 5)	6.5 (2 H, d, J 9.0) and 8.0 (2 H, d, J 9.1) C <sub>6</sub> H <sub>4</sub> Me; 2.8 (s) N(CH <sub>3</sub> ) <sub>2</sub> ; 2.2 (s) CH <sub>3</sub>
2a	6.9 (s)	3.2 (m)	1.8 (q, J 6)	2.8 (s) CH <sub>3</sub>
2c	6.9 (s)	3.1 (m)	1.7 (m)	7.3 (s) C <sub>6</sub> H <sub>5</sub> ; 4.1 (s) CH <sub>2</sub> Ph
2d	7.5 (s)	3.5 (m)	2.0 (q, J 6)	7.1 (m) C <sub>6</sub> H <sub>5</sub>
2e	7.7 (s)	3.6 (m)	2.0 (q, J 6)	7.2 (2 H, d, J 9.0) and 8.2 (2 H, d, J 9.1) C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>
2f	7.4 (s)	3.4 (m)	1.9 (q, J 6)	6.5 (2 H, d, J 7.0) and 6.8 (2 H, d, J 7.1) C <sub>6</sub> H <sub>4</sub> Me; 2.3 (s) CH <sub>3</sub>
2g	6.7 (s)	3.2 (m)	1.7 (q, J 6)	3.3 (s) OCH <sub>3</sub> ; 3.1-3.5 (m) -CH <sub>2</sub> -CH <sub>2</sub> -
3	6.9 (s)	3.2 (m)	1.8 (t, J 6)	3.1 (s, bridge)
3'	6.7 (s)	3.1 (m)	1.8 (m)	1.8 (m, bridge)
4a	7.9 (s)	3.4 (t J 6)	2.2 (q, J 6)	3.2 (s) Me
4c	9.3 (s)	3.3 (m)	2.1 (m)	7.2 (m) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ; 4.7 (s) PhCH <sub>2</sub> ; 4 (s) Me
4d	8.4 (s)	3.5 (t, J 6)-3.8 (t, J 6)	2.3 (q, J 6)	7.5 (s) C <sub>6</sub> H <sub>5</sub> ; 3.2 (s) Me
4e	8.7 (s)	3.6 (t, J 6)-3.9 (t, J 6)	2.3 (m)	7.3 (2 H, d, J 8.5) and 8.3 (2 H, d, J 8.5) C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ; 3.4 (s) Me
4f	8.3 (s)	3.4 (t, J 6)-3.7 (t, J 6)	2.2 (t, J 6)	7.3 (2 H, d, J 8.5) and 8.3 (2 H, d, J 8.5) C <sub>6</sub> H <sub>4</sub> Me; 2.4 (s) Me; 3.3 (s) C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>
4g	7.0 (s)	3.5 (t, J 6)	1.6 (m)	2.6 (t, J 7) CH <sub>2</sub> CH <sub>2</sub> OMe; 2.8 (t, J 7) CH <sub>2</sub> CH <sub>2</sub> OMe; 3.3 (s) Me
4h	8.9 (s)	3.7 (t J 6)	2.2 (q, J 6)	3.4 (s) Me; 3.5 (q, J 7); CH <sub>2</sub> CH <sub>3</sub> ; 1.3 (t, J 7); CH <sub>2</sub> CH <sub>3</sub>
4i	8.6 (s)	3.3 (t, J 6)	2.1 (m)	8.6 (s) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ; 4.7 (s) PhCH <sub>2</sub>
5a	8.4 (s)	3.4 (m)	2.3 (m)	4.1 (s, bridge); 3.6 (s) CH <sub>3</sub>
5b	8.6 (s)	3.7 (m)	2.5 (m)	4.3 (s, bridge); 1.6 (t, J 7) CH <sub>3</sub> ; 3.6 (m) CH <sub>2</sub> -CH <sub>2</sub> -
5a'	8.0 (s)	3.5 (m)	2.3 (m)	CH <sub>3</sub> 3.3 (s)
5b'	8.8 (s)	4.3 (t, J 6)	3.0 (m)	2.3 (t, J 7) CH <sub>3</sub> ; 4.3 (m) -CH <sub>2</sub> -
5c'	8.7 (s)	3.9 (m)	2.5 (m)	7.7 (s) C <sub>6</sub> H <sub>5</sub> ; 5.0 (s) Ph-CH <sub>2</sub>

<sup>†</sup> Spectra recorded in CDCl<sub>3</sub> and D<sub>2</sub>O at 60 and 80 MHz and 305 K; Chemical shifts (δ) relative to Si(CH<sub>3</sub>)<sub>4</sub> = 0.

**Table 3**  $^{13}\text{C}$  Nmr spectroscopic data with assignments for 1, 2, 3, 4 and 5.\*

Compound No	2 -	4.6 -	5 -	Others
4a	137.1	35.7	14.9	$\text{CH}_3$ 38.5
4c	140.8	26.8	23.7	$\text{C}_6\text{H}_5$ 135.0, 130.4, 130.1, 129.9; $\text{C}_6\text{H}_5\text{CH}_2$ 58.4; $\text{CH}_3$ 44.0
4d	153.8	43.8, 44.1	19.4	$\text{C}_6\text{H}_5$ 123.6, 129.2, 130.9, $\text{CH}_3$ 46.1
4e	168.5	55.6, 55.2	40.0	$\text{C}_6\text{H}_4$ 122.5, 123.0, 137.6, 138.2; $\text{CH}_3$ 46.6
4f	151.7	45.4, 45.6	18.6	$\text{C}_6\text{H}_4$ 138.6, 137.9, 130.1, 121.9; $\text{C}_6\text{H}_4\text{CH}_3$ 20.6; $\text{CH}_3$ 43.1
4h	140.5	36.5	28.6	$\text{CH}_2\text{CH}_3$ 5.6, $\text{CH}_3\text{CH}_2$ 29.2, $\text{CH}_3$ 32.0
4i	156.5	43.9	20.9	$\text{C}_6\text{H}_5$ 118.5, 113.9; 113.3; $\text{C}_6\text{H}_5\text{CH}_2$ 40.5
5a	154.1	42.8, 43.5	19.3	$-\text{CH}_2$ (bridge) 52.7; $\text{CH}_3$ 45.5
5b	153.8	44.3, 42.9	18.8	$-\text{CH}_2$ (bridge) 52.4, $\text{CH}_2\text{CH}_3$ 50.9; $\text{CH}_2\text{CH}_3$ 13.1
5a'	153.4	44.3, 43.5	19.1	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (bridge) 25.4; $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (bridge) 49.4; $\text{CH}_3$ 44.6
5b'	152.7	44.0, 43.6	18.9	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (bridge) 26.2; $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (bridge) 50.9; $\text{CH}_2\text{CH}_3$ 53.1; $\text{CH}_2\text{CH}_3$ 13.8
5c'	153.2	43.3	19.6	$\text{C}_6\text{H}_5$ 128.8, 129.5, 130.2, 134.5; $\text{C}_6\text{H}_5\text{CH}_2$ 60.5; $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (bridge) 19.6; $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (bridge) 43.3

\* Spectra recorded in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  at 305 K.

salts (**5**) could be prepared *via* the route iv or route v by using **3** or **2**, but the yields are higher in the case of route iv (Scheme 1). The new salts were characterized by elemental analysis and nmr spectroscopy (Tables 2 and 3). In the  $^1\text{H}$  nmr spectra, H2 resonances were relatively broad and diagnostic. Comparison of the signals in the free pyrimidines and the corresponding salts clearly indicates that the formation of the salt increases the acidity of the C-2 proton. Consistent with this, NaH reacts with the salts (**5**) to produce the pyrimidine skeleton containing tetraaminoalkenes.<sup>6</sup> This observation provides further evidence for the proposed structures of the salts. The bridged salts (**5**) where  $\text{R}' = \text{CH}_2\text{C}_6\text{H}_4.\text{CH} = \text{CH}_2\text{-}p$  were used as monomers.<sup>18</sup>

The attempted dehydrogenation of **2c** with sulfur led to insertion of sulfur on the molecule to give the 1,4,5,6-tetrahydro-2-mercaptopyrimidine (**6c**) as colorless needles. **6c** ( $\text{R} = \text{CH}_2\text{Ph}$ ) is identical with the compound which was obtained from the reaction of 1-benzyl-1,3-propanediamine with carbon disulfide.<sup>12</sup>

1,4,5,6-Tetrahydropyrimidine and 1-ethyl-1,4,5,6-tetrahydropyrimidine (**2**;  $\text{R} = \text{H}$  and Et) respectively, have been prepared previously in moderate yields by the reactions of 1,3-propanediamines with liquid HCN under forcing conditions.<sup>19</sup>

In order to compare the cyclization efficacy of the acetal with other acid derivatives we treated 1-substituted 1,3-diaminopropanes with (A)  $\text{Me}_2\text{NCH}(\text{OMe})_2$  and (B)  $\text{HC}(\text{OEt})_3$  and tabulated the isolated yields in Table 4 with that of acetamide (method C).<sup>12</sup> It can be seen that the simple work-up, isolation of pure products without chromatographic separation, high yields and use of safe and cheap reagents with no special handling techniques are the notable advantages of the present method.

Table 4 Comparison of the Methods for the Preparation of 1-Substituted 1,4,5,6-Tetrahydropyrimidine.

Compound No	Method A <sup>a</sup>		Method B <sup>b</sup>		Method C <sup>c</sup>	
	Time	Yield (%)	Time	Yield (%)	Time	Yield (%)
<b>2</b> <sup>d</sup>	½ h	90	52 h	36	2 h	85
<b>2a</b>	½ h	95	52 h	-	2 h	95
<b>2c</b>	½ h	90	52 h	67	2 ½ h	90
<b>2d</b>	½ h	91	52 h	48	-	-
<b>2e</b>	1 h	80	50 h	-	-	-
<b>2f</b>	1 h	72	52 h	57	-	-
<b>2g</b>	½ h	82	-	-	-	-

<sup>a</sup> Condensation of *N,N*-dimethylformamide dimethylacetal with 1-substituted 1,3-propanediamines.

<sup>b</sup> Condensation of triethyl orthoformate with 1-substituted 1,3-propanediamines. <sup>c</sup> Reaction of formamide acetate with 1-substituted 1,3-propanediamines. <sup>d</sup> (**2**,  $\text{R} = \text{H}$ )

## EXPERIMENTAL

All operations were carried out under an atmosphere of dry by using standard Schlenk or vacuum-line techniques. Solvents were purified by the usual method before use.<sup>20</sup> Mps were obtained with an electrothermal apparatus and uncorrected. C, H, N analyses were carried out in the Middle East Technical University Laboratory - Ankara with a Hewlett - Packart Model 185 analyzer. Ir spectra were recorded with Hitachi Model 200 as KBr discs. <sup>1</sup>H Nmr spectra were determined as solution in CDCl<sub>3</sub> unless otherwise noted on a Bruker - AC80F T spectrometer.

*Preparation of the N-methyl-1,4,5,6-tetrahydropyrimidine (2a).*- *N,N* - Dimethylformamide dimethylacetal<sup>15</sup> (6.3 g, 52.9 mmol) was added to *N*-methyl-1,3-diaminopropane (4.2 g, 47.9 mmol). The mixture was stirred at 90°C for 0.5 h, heated to 110°C for 0.5 h and **2a** was purified by distillation as an oil (4.5 g 95%). The compounds (**2b**, **2c**, **2g**, **3**, **3'**) were obtained by similar method.

*Preparation of 1-(p-nitrophenyl)-2-dimethylamino-hexahydropyrimidine (1e).*- *N,N* - Dimethylformamide dimethylacetal (1.8 g, 15.1 mmol) was added to *N*-(*p*-nitrophenyl)-1,3-diaminopropane (2.5 g, 12.8 mmol). The mixture was stirred at 90°C for 0.5 h. Volatiles were removed under reduced pressure. The yellow oily residue was crystallized from toluene (4 ml) at -20°C, (3.44 g, 85%). The compounds (**1d**) and (**1f**) were obtained by similar method.

For the preparation of compound (**2e**), neat **1e** (4.0 g, 16.0 mmol) was heated at 190-200°C for 0.5 h. Yellow oily residue was crystallized from toluene / hexane (2 / 1) at -20°C to give yellow crystals of **2e** (2.8 g, 80%).

*Preparation of N,N'-dimethyl-1,4,5,6-tetrahydropyrimidinium iodide (4a).*- To a solution of *N*-methyl-1,4,5,6-tetrahydropyrimidine (**2a**) (3.76 g, 37.2 mmol) in THF (10 ml), iodomethane (5.28 g, 37.2 mmol) was added slowly. The mixture was stirred at 20°C for 10 h. A white solid precipitated which was filtered off and recrystallized from ethyl alcohol/ether (8 / 5 ml), (7.8 g, 85%). Compounds (**4c**, **4d**, **4e**, **4f**, **4h**, **4i**) were obtained by similar procedure.

*Preparation of the 1,1'-dimethylene-3,3'-dimethylbis(1,4,5,6-tetrahydropyrimidinium) diiodide (5a).* - *Method (iv).*- 1,1'-Dimethylenebis(1,4,5,6-tetrahydropyrimidine) (**3**) (4.24 g, 21.6 mmol) and iodomethane (6.13 g, 43.2 mmol) were stirred in 20 ml of DMF at 20°C for 8 h. Ether (2x10 ml) was added and the solid formed was filtered off. The white solid was washed with ether (2x20 ml), dried under vacuum, (8.8 g, 81%). The compounds (**5b**, **5a'**, **5b'**, **5c'**) were obtained by similar procedure.

*Method (v).*-1,2-Dibromoethane (26.2 g, 119.4 mmol) was added to *N*-methyl-1,4,5,6-tetrahydropyrimidine (**2a**) (23.5 g, 239.4 mmol) in DMF (60 ml). The mixture was stirred at 20°C for 10 h, ether (40 ml) was added to precipitate (**5a**). The white solid (**5a**) was filtered off and washed with ether (2x20 ml) and dried under vacuum (7.7 g, 17%).

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Received, 1st, May, 1996