($CHCl_3$) 1665, 1462, 1440, 1385, 1380, 950, 934, and 900 cm^{-1}; NMR (C_6D_6) δ 6.87 (d of q, 1, J = 13, 7 Hz), 5.92 (d of broad peaks, 1, J = 13 Hz), 2.87 (s, 6), and 1.45 (d of d, 3, J = 7, 2 Hz).

***N,N*-Dimethylvinylamine *N*-Oxide (3c).** This was prepared similarly to **3a** to give **3c** in 52% yield as deliquescent, white, feathery crystals: mp 96–100 °C; decomposition temp, 145 °C; IR ($CHCl_3$) 1650, 1465, 1450, 952, 910, and 895 cm^{-1}; NMR (C_6D_6) δ 6.3–6.1 (m, 2), 4.9–4.7 (m, 1), and 2.85 (s, 6).

Reactions of *N,N*-Dimethyl-1-cyclohexenylamine *N*-Oxide (3a). General. Except where noted, the reactions of **3a** were run under an atmosphere of nitrogen or argon either on an aliquot of **3a** in *tert*-butyl alcohol or on a sublimed sample of **3a** dissolved in benzene-d_6 in an NMR tube. Reactions were monitored by NMR spectroscopy and worked up by addition of water and extraction with $CHCl_3$. The $CHCl_3$ extract was washed with saturated NaCl and dried ($MgSO_4$ or $CaSO_4$). The products were isolated by VPC and identified by comparison of VPC retention times and spectra with those of authentic samples. The authentic samples were obtained commercially, as gifts,[18] or by synthesis using known routes. Yields are based on comparison of the VPC peak area of a known amount of hydrocarbon standard, which had been added to the reaction mixture before workup, with the product peak areas, which had been corrected by determination of the response factor of the authentic sample vs. the hydrocarbon standard.

VPC Decomposition of 3a. Injection of part of a solution containing 38.9 mg (0.28 mmol) of **3a** and 11.2 mg (0.061 mmol) of *n*-tridecane (as standard) in 0.25 mL of benzene-d_6 onto a column packed with silicone rubber UC-W98 with an injection port temperature of 270 °C and a thermal conductivity detector temperature of 230 °C gave cyclohexanone (6%), *N,N*-dimethyl-1-cyclohexenylamine (**11**; 20%), and 2-dimethylaminocyclohexanone (13%) as the major products. Coinjection of water with the sample resulted in an enhanced yield of cyclohexanone and the disappearance of **11**. Similar results were obtained at an injection port temperature of 170 °C.

Reaction of 3a with Acetic Anhydride. A 71.4-mg (0.51 mmol) sample of **3a** was treated with 57 mg (0.56 mmol) of acetic anhydride to give, after aqueous workup, cyclohexanone (4%), *N,N*-dimethylacetamide (20%), and 2-acetoxycyclohexanone (78%). Similar results were obtained when the reaction was run in *tert*-butyl alcohol or $CHCl_3$.

Reaction of 3a with Benzoyl Chloride. A 73.7-mg (0.522 mmol) sample of **3a** was treated with 80.6 mg (0.57 mmol) of benzoyl chloride to give, after aqueous workup, cyclohexanone (2%), 2-chlorocyclohexanone (25%), benzoic acid (46%), *N,N*-dimethylbenzamide (32%), and 2-benzoxycyclohexanone (20%).

Reaction of 3a with Diketene. A 50.7-mg (0.36 mmol) sample of **3a** was treated with 30.3 mg (0.36 mmol) of diketene (freshly distilled) to give, after aqueous workup with dilute HCl, cyclohexanone (15%), *N,N*-dimethylacetoacetamide (15%), and 2-acetonylcyclohexanone (14%) as the major products.

Reaction of 3a with Trifluoroacetic Anhydride. To a 46.0-mg (0.33 mmol) sample of **3a** in 1 mL of CD_2Cl_2 at −78 °C was added 68.5 mg (0.33 mmol) of trifluoroacetic anhydride. A yellow color formed immediately and gradually turned dark orange. After aqueous workup, the major products identified were 2-trifluoroacetoxycyclohexanone (32%) and cyclohexanone (18%).

Reaction of 3a with *n*-Butyllithium. A 55.8-mg (0.40 mmol) sample of **3a** was treated with 0.25 mL (0.40 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After shaking the reaction mixture for 10 min, 0.5 mL of D_2O was added. NMR analysis of the aqueous phase indicated the presence of some unreacted **3a**. Aqueous workup gave cyclohexanone (48%). The presence of formaldehyde in the aqueous phase was inferred from a VPC retention time comparison with a formalin solution on a column packed with Carbowax 20M (flame ionization detector).

Reaction of 3a with Titanium Tetrachloride. To a 34.4-mg (0.24 mmol) sample of **3a** was added 26.8 mg (0.24 mmol) of titanium tetrachloride at 0 °C. The solution turned brown immediately. After aqueous workup, the major products were 2-chlorocyclohexanone (47%) and cyclohexanone (19%).

Acknowledgment. The authors gratefully acknowledge the advice of Professor Glenn A. Berchtold during this study and his reading of the manuscript.

Registry No.—**1a,** 4580-81-8; **1b,** 108-14-5; **1c,** 107-99-3; **2a** HCl, 66172-49-4; **2a** picrate, 66172-51-8; **2b** HCl, 66172-52-9; **2b** picrate, 66172-54-1; **2c** HCl, 66172-55-2; **3a,** 66172-56-3; **3a** picrate, 66172-57-4; **3b,** 66172-58-5; **3c,** 66172-59-6; cyclohexanone, 108-94-1; *N,N*-dimethylacetamide, 127-19-5; 2-acetoxycyclohexanone, 17472-04-7; 2-chlorocyclohexanone, 822-87-7; benzoic acid, 65-85-0; *N,N*-dimethylbenzamide, 611-74-5; 2-benzoxycyclohexanone, 7472-23-3; *N,N*-dimethylacetoacetamide, 2044-64-6; 2-acetonylcyclohexanone, 6126-53-0; 2-trifluoroacetoxycyclohexanone, 66197-69-1.

References and Notes

(1) (a) Technicon Instruments Corp., Tarrytown, N.Y. 10591; (b) Universidad Nacional Experimental del Tachira, Venezuela.
(2) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds", Vol II, W. A. Benjamin, New York, N.Y., 1966, pp 21–28.
(3) A. C. Cope and E. R. Trumbull, *Org. React.*, **11**, 317 (1960).
(4) G. A. Russel and G. J. Mikol, *Mech. Mol. Migr.*, **1**, 157 (1968).
(5) R. A. W. Johnstone, *Mech. Mol. Migr.*, **2**, 249 (1969).
(6) "Enamines: Synthesis, Structure, and Reactions", A. G. Cook, Ed., Marcel Dekker, New York, N.Y., 1969.
(7) E. M. Volker, M.S. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1967.
(8) F. L. Lam and G. A. Berchtold, unpublished results.
(9) R. R. Renshaw and J. C. Ware, *J. Am. Chem. Soc.*, **47**, 2989 (1925).
(10) B. Hansen, *Acta Chem. Scand.*, **17**, 1483 (1963).
(11) The preparation of **2c** from **1c** with peracetic acid has been reported by Y. Sakurai and M. Izumi, *Pharm. Bull.*, **1**, 297 (1953).
(12) J. Sauer and H. Prahl, *Tetrahedron Lett.*, 2863 (1966), reported 13.6 and 8.8 Hz for *N,N*-dimethyl-*trans*-1-propenylamine and *N,N*-dimethyl-*cis*-1-propenylamine, respectively.
(13) R. D. Haworth and W. H. Perkin, *J. Chem. Soc.*, 1769 (1926).
(14) E. Bamberger and P. Leyden, *Ber.*, **34**, 12 (1901).
(15) A. Ahond, A. Cave, C. Kan-Fan, H. P. Husson, J. De Rostolan, and P. Potier, *J. Am. Chem. Soc.*, **90**, 5622 (1968), and preceeding papers.
(16) M. L. Loeb, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1969.
(17) F. Minisci, R. Galli, and G. Pollina, Chim. Ind. (Milan), **47**, 736 (1965).
(18) A sample of 2-acetoxycyclohexanone was kindly provided by Professor H. O. House.

Synthesis of N,N,N′,N′-Tetrasubstituted 1,1-Diaminoethylenes and Their Thermal Rearrangement

Yoshiro Sato,* Masami Kato, Toyohiko Aoyama, Michiharu Sugiura, and Hideaki Shirai

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

Received November 21, 1977

Various N,N,N′,N′-tetrasubstituted 1,1-diaminoethylenes (**5**) have been prepared by the reaction of N,N-disubstituted (trimethylsilylethynyl)amines (silylynamines **1**, **2**, and **3**) with secondary amines. At 200 °C in amine solvent, **5** afforded a mixture of [1,3] alkyl rearrangement products (**7**) and dealkylation products (**8** and/or **9**).

N,N,N′,N′-Tetrasubstituted 1,1-diaminoethylenes are the simplest enamines having two tertiary amino groups on the same carbon and may be useful intermediates for organic synthesis. Several 1,1-bis(disubstituted amino)ethylenes have been prepared by the reaction of a secondary amine with a ketene acetal[1] or triethyl orthoacetate,[2] dimethylacetamide

0022-3263/78/1943-2466$01.00/0

Table I. Reaction of Silylynamine (1, 2, and 3) with Secondary Amines (4)

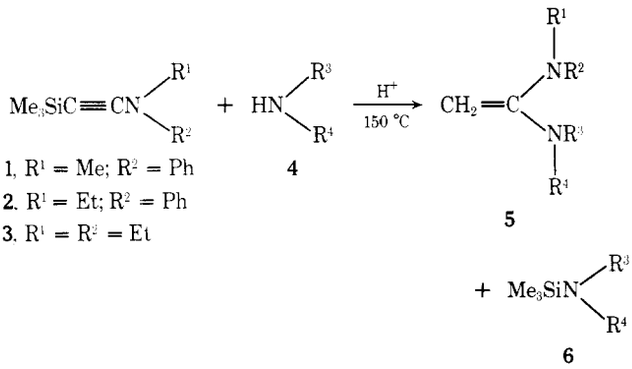
Run	Starting material: Silylynamine R^1	Silylynamine R^2	Secondary amine R^3	Secondary amine R^4	Reaction time, h	Catalyst[a]	Yield of 5, %	Compd No.
1	Me	Ph	Me	Ph	1	H^+	84	**5a**
2	Me	Ph	Et	Et	10	H^+	89	**5b**
3	Me	Ph	Et	Ph	1	H^+	78	**5c**
4	Me	Ph	*n*-Pr	Ph	3	H^+	80	**5d**
5	Me	Ph	*i*-Pr	Ph	3	H^+	63	**5e**
6	Me	Ph	Allyl	Ph	3	H^+	68	**5f**
7	Me	Ph	*n*-Bu	*n*-Bu	6	H^+	61	**5g**
8	Et	Ph	Me	Ph	1	H^+	88	**5c**
9					13		73	**5c**
10	Et	Ph	Et	Et	10	H^+	85	**5h**
11	Et	Ph	Et	Ph	2	H^+	84	**5i**
12					24		81	**5i**
13	Et	Ph	*n*-Pr	Ph	3	H^+	75	**5j**
14	Et	Ph	Allyl	Ph	2	H^+	66	**5k**
15	Et	Et	Me	Ph	1	H^+	84	**5b**
16					24		0	
17	Et	Et	Et	Et	10	H^+	82	**5l**
18	Et	Et	Et	Ph	2	H^+	75	**5h**
19	Et	Et	*i*-Pr	Ph	2	H^+	78	**5m**
20	Et	Et	Cyclohexyl	Ph	2	H^+	85	**5n**

[a] *N*-Methylaniline hydrobromide, 0.53 mol %.

Table II. N,N,N′,N′-Tetrasubstituted 1,1-Diaminoethylenes (5)[a]

	Bp (mmHg), °C	IR(film), cm^{-1} (C=C)	NMR ($CDCl_3$), δ (CH_2=C<)
5a	118–120 (0.5)	1630	4.08 (s)
5b	138–140 (18)	1620	3.71 (s)
5c	120–122 (0.4)	1625	4.10 and 4.17 (AB, q)
5d	128–130 (0.7)	1625	4.11 and 4.18 (AB, q)
5e	125–127 (0.7)	1625	3.97 (s)
5f	132–134 (0.6)	1620	4.16 and 4.29 (AB, q)
5g	134–136 (2)	1620	3.67 (s)
5h	145–147 (20)	1620	3.74 and 3.78 (AB, q)
5i	115–117 (0.3)	1625	4.08 (s)
5j	135–137 (1)	1625	4.04 (s)
5k	120–122 (0.2)	1620	4.18–4.23 (AB, q)
5l[b]	92–94 (40)	1625	3.38 (s)
5m	91–92 (0.8)	1615	3.65 and 3.80 (AB, q)
5n	108–110 (0.3)	1615	3.66 and 3.80 (AB, q)

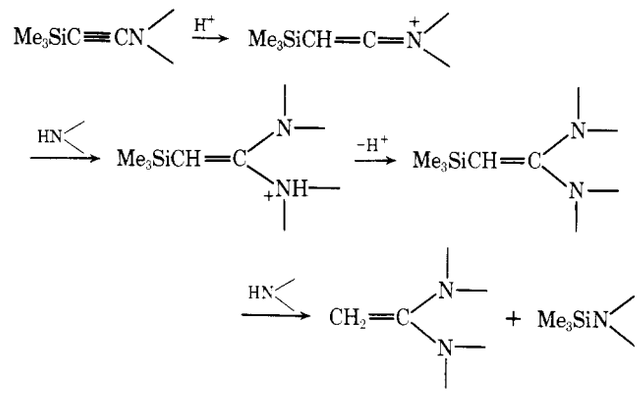
[a] Satisfactory analytical data (±0.4 for C, H, and N) were reported for all new compounds listed in the table. [b] Lit. bp 89–93 °C (40 mmHg), ref 1.



1, R^1 = Me; R^2 = Ph
2. R^1 = Et; R^2 = Ph
3. R^1 = R^2 = Et

4

with tetrakis(dimethylamino)titanium,[3] and tetramethylacetamidinium salt with sodium hydride.[4] These procedures have been examined for the preparation of symmetrical 1,1-diaminoethylenes, but it seems difficult to apply these to the synthesis of asymmetrical ones. In this paper, we report a new synthetic route of various types of asymmetrical N,N,N′,N′-tetrasubstituted 1,1-diaminoethylenes (**5**) by reaction of N,N-disubstituted (trimethylsilylethynyl)amines (silylynamines, **1**, **2**, and **3**)[5] with secondary amines and the thermal rearrangement of **5**.



Heating of silylynamines (**1**, **2**, and **3**) in an appropriate secondary amine at 150 °C gave the corresponding 1,1-diaminoethylenes **5** in good yields. Yields and characterizing data are summarized in Tables I and II. Addition of a catalytic amount of *N*-methylaniline hydrobromide to the reaction mixture accelerated the reaction (compare runs 8 and 9, or runs 11 and 12, in Table I). *N,N*-Diethyl(trimethylsilylethynyl)amine (**3**) did not react with a secondary amine in the

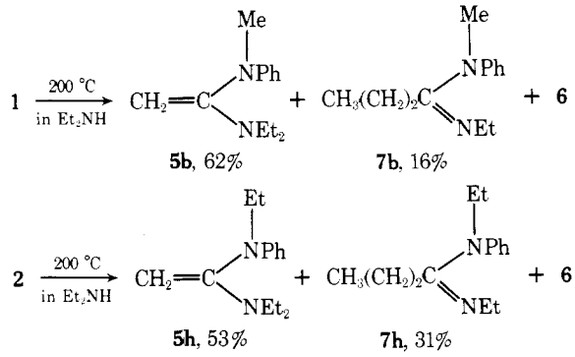
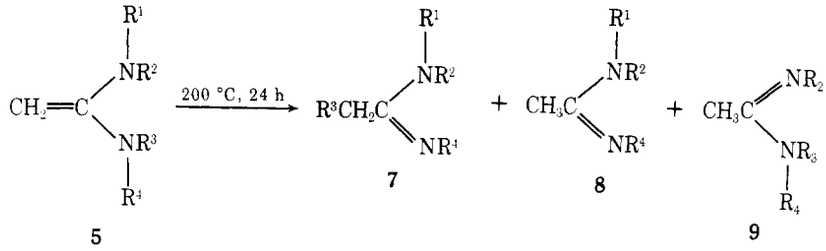


Table III



Run		R1	R2	R3	R4	Solvent[a]	Yield, % Without DTBP 7	8	9	With DTBP 7	8	9
1	a	Me	Ph	Me	Ph	A	0	39		0	42	
2						B				0	8	
3	b	Me	Ph	Et	Et	A	28	0	7	37	0	0
4						C				24	0	0
5	c	Me	Ph	Et	Ph	A	34	8	31	46	0	0
6						B	0	0	0	39	0	0
7						C				34	0	0
8	d	Me	Ph	*n*-Pr	Ph	A				28	5	34
9	f	Me	Ph	Allyl	Ph	B	80	0	0			
10	h	Et	Ph	Et	Et	A				32	0	0
11	i	Et	Ph	Et	Ph	A	60	0		64	0	
12						B	0	0		45	13	
13						D	0	0		16	30	

[a] A = diethylamine, B = triethylamine, C = piperidine, D = diisopropylamine.

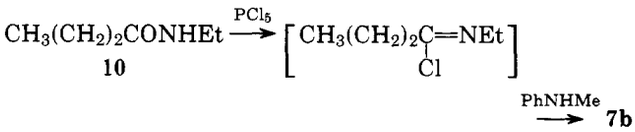
Table IV. Physical Properties of Amidines (7, 8, and 9)[a]

	Bp (mmHg), °C	IR (film), cm^{-1} (C=N)	NMR ($CDCl_3$), δ
7b	125–126 (22)	1625	0.74 (t, 3, $CH_3CH_2CH_2$), 1.22 (t, 3, NCH_2CH_3), 1.12–1.50 (m, 2, $CH_3CH_2CH_2$), 2.06–2.26 (m, 2, CH_2C), 3.18 (s, 3, NCH_3), 3.36 (q, 2, NCH_2), 7.00–7.50 (m, 5, aromatic H)
7c	138–140 (0.4)	1620	0.50 (t, 3, CH_3CH_2), 1.03–1.40 (m, 2, $CH_3CH_2CH_2$), 2.06–2.25 (m, 2, CH_2C), 3.33 (s, 3, NCH_3), 6.60–7.40 (m, 10, aromatic H)
7d	140–143 (0.8)	1620	0.50 (t, 3, CH_3CH_2), 0.70–1.38 (m, 4, $CH_3CH_2CH_2CH_2$), 2.06–2.30 (m, 2, CH_2C), 3.36 (s, 3, NCH_3), 6.70–7.60 (m, 10, aromatic H)
7f	121–123 (0.1)	1615	1.80–2.08 (m, 2, $=CHCH_2$), 2.12–2.40 (m, 2, CH_2C), 3.32 (s, 3, NCH_3), 4.48–4.80 (m, 2, $CH_2=$), 5.10–5.60 (m, 1, =CH–), 6.70–7.50 (m, 10, aromatic H)
7h	102–104 (10)	1620	0.72 (t, 3, $CH_3CH_2CH_2$), 1.06 (t, 3, $=NCH_2CH_3$), 1.20 (t, 3, NCH_2CH_3), 1.00–1.44 (m, 2, $CH_3CH_2CH_2$), 2.00–2.20 (m, 2, CH_2C), 3.34 (q, 2, $=NCH_2$), 3.73 (q, 2, NCH_2), 7.00–7.50 (m, 5, aromatic H)
7i	128–130 (0.5)	1620	0.50 (t, 3, $CH_3CH_2CH_2$), 1.20 (t, 3, NCH_2CH_3), 1.04–1.44 (m, 2, $CH_3CH_2CH_2$), 2.00–2.20 (m, CH_2C), 3.89 (q, 2, NCH_2), 6.80–7.60 (m, 10, aromatic H)
8a,c,d	89–92 (0.03)[b]	1625	1.66 (s, 3, CH_3C), 3.37 (s, 3, NCH_3), 6.70–7.48 (m, 10, aromatic H)
8i, 9c	96–97 (0.03)[c]	1610	1.20 (t, 3, NCH_2CH_3), 1.64 (s, 3, CH_3C), 3.92 (q, 2, NCH_2), 6.77–7.50 (m, 10, aromatic H)
9b	88–93 (0.4)	1610	1.27 (t, 6, $NCH_2CH_3 \times 2$), 1.78 (s, 3, CH_3C), 3.36 (q, 4, $NCH_2 \times 2$), 6.47–7.30 (m, 5, aromatic H)
9d	112–113 (0.13)	1620	0.88 (t, 3, $CH_3CH_2CH_2$), 1.60 (s, 3, CH_3C), 1.60 (m, 2, NCH_2CH_2), 3.81 (m, 2, NCH_2), 6.60–7.50 (m, 10, aromatic H)

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] Lit.[7] bp 320–324 °C. [c] Lit.[8] bp 190–192 °C (15 mmHg).

absence of the proton catalyst (run 16). The presence of proton catalyst may assist the attack of a secondary amine to α carbon of the ynamine.

When the reaction was carried out without proton catalyst at high temperature, the reaction was complicated by competitive formation of isomers of **5**. For example, heating of **1** or **2** in an excess of diethylamine at 200 °C gave the corresponding 1,1-diaminoethylene **5b** or **5h** and its isomeric product **7b** or **7h**. The NMR spectra of **7b** and **7h** exhibited a typical signal pattern of the *n*-propyl group instead of that of the external methylene group in **5b** and **5h**. These data would be consistent with structures of *N*-methyl(or ethyl)-*N*-phenyl-*N'*-ethylbutyramidine (**7b** and **7h**). Compound **7b** was identical by spectroscopic comparison with an authentic sample prepared from *N*-ethylbutyramide (**10**) and *N*-methylaniline.



Amidine **7** may be formed by [1,3] rearrangement of an ethyl group from nitrogen to carbon in the initially formed **5**. Actually, heating of **5b** in diethylamine at 200 °C gave a 28% yield of **7b** (run 3 in Table III). Other 1,1-diaminoethylenes **5c** and **5i** also gave the corresponding rearrangement products **7c** and **7i** under the same reaction condition (runs 5 and 11). These ethyl migrations proceeded smoothly in diethylamine but not in triethylamine. However, in the presence of a catalytic amount of DTBP, the *N*-ethyl or *N*-*n*-propyl group of **5** migrated to give the corresponding butyr- or hexanamidine derivative in triethylamine (runs 6 and 12). The *N*-methyl group in **5** did not migrate to give the corresponding propionamidine derivatives in any cases, but the demethylation products **8** or **9** were formed.

Thermal [1,3] alkyl rearrangement may occur either by a sigmatropic shift following a suprafacial path with inversion at the migrating center or by a radical dissociation–recombination path.[6] The accelerating effect of DTBP, mentioned above, seems to suggest that the transformation of **5** to **7** proceeds via radical intermediates. From the present results, however, we cannot conclude it. 1-Allylphenylamino-1-methylphenylaminoethylene (**5f**) was converted into *N,N'*-diphenyl-*N*-methyl-4-pentenamidine (**7f**) in a high yield by heating without the aid of DTBP (run 9 in Table III).

Experimental Section

All boiling points are uncorrected. NMR spectra were recorded using a JEOL Model JNM-MH-100 spectrometer employing Me_4Si as internal standard. IR spectra were taken on a JASCO Model IRA-2 spectrometer. GLC analyses were performed on a JEOL Model JGC-1100 FID chromatograph. Fractional distillation was accomplished by a Büchi Model GKR-50 Kugelrohr distillation apparatus. All solvents were distilled in a nitrogen atmosphere just prior to use and the reactions were carried out under nitrogen atmosphere.

N,N,N',N'-Tetrasubstituted 1,1-Diaminoethylenes (5). A mixture of 10 mmol of silylynamine [*N*-methyl-*N*-(trimethylsilylethynyl)aniline (**1**), *N*-ethyl-*N*-(trimethylsilylethynyl)aniline (**2**), or *N,N*-diethyl(trimethylsilylethynyl)amine (**3**)],[5] 30 mmol of secondary amine, and 10 mg (0.53 mol %) of *N*-methylaniline hydrobromide was heated with stirring at 150 °C for 1–10 h. The reaction mixture was distilled under reduced pressure to give the corresponding **5**.

The yields and characterizing data are summarized in Tables I and II.

Thermal Reaction of 5. A solution of 7 mmol of **5** in 2 mL of amine (diethylamine, triethylamine, diisopropylamine, or piperidine) was heated with 100 mg (10 mol %) of DTBP (or without DTBP) in a sealed tube at 200 °C for 24 h. The reaction mixtures were analyzed by GLC using a 3 mm × 1 m stainless steel column filled with 10% silicone SE-30, and the yields were determined by the internal standard method. Samples of the products were isolated by fractional distillation of the reaction mixtures. The yields and characterizing data are shown in Tables III and IV.

***N*-Methyl-*N*-phenyl-*N'*-ethylbutyramidine (7b).** To a chilled suspension of PCl_5 (5.6 g, 27 mmol) in dry chloroform (30 mL) was added dropwise *N*-ethylbutyramide (2.6 g, 23 mmol) and stirring was continued for 15 min. Then a solution of *N*-methylaniline (2.42 g, 23 mmol) in chloroform (5 mL) was added and the mixture was stirred for 2 h at room temperature and an additional 2 h at reflux. After the addition of water (50 mL) to the reaction mixture, the aqueous layer was separated and made alkaline with NaOH solution and then extracted with ether. The ethereal extract was dried, concentrated, and distilled to give 1.60 g (35%) of **7b**, bp 120–122 °C (20 mm).

Acknowledgment. The authors are grateful to the Shin-Etsu Chemical Industry Co., Ltd., for a generous gift of chlorosilanes. We also wish to thank Dr. T. Konaka, Shionogi Research Laboratory, for helpful discussions.

Registry No.—*N*-Ethylbutyramide, 13091-16-2.

References and Notes

(1) S. M. McElvain and B. E. Tate, *J. Am. Chem. Soc.*, **67**, 202 (1945).
(2) H. Baganz and L. Domaschke, *Chem. Ber.*, **95**, 2095 (1962).
(3) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).
(4) C. Jutz and H. Amschler, *Chem. Ber.*, **96**, 2100 (1963).
(5) For the preparation of silylynamines, see Y. Sato, Y. Kobayashi, M. Sugiura, and H. Shirai, *J. Org. Chem.*, **43**, 199 (1978).
(6) C. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).
(7) L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 777 (1941).
(9) J. v. Braun, F. Jostes, and A. Heymons, *Ber.*, **60**, 92 (1927).

Preparation of the Enantiomeric Forms of 9-(5,6-Dideoxy-β-D-*ribo*-hex-5-enofuranosyl)adenine[1]

Leon M. Lerner

Department of Biochemistry, State University of New York, Downstate Medical Center, Brooklyn, New York 11203

Received November 17, 1977

D-Allose was converted to methyl 2,3:5,6-di-*O*-isopropylidene-β-D-allofuranoside, and this in turn was hydrolyzed in an acid solution to methyl 2,3-*O*-isopropylidene-β-D-allofuranoside. Treatment of the latter with methanesulfonyl chloride gave methyl 2,3-*O*-isopropylidene-5,6-bis(*O*-methanesulfonyl)-β-D-allofuranoside. The latter was treated with sodium iodide to afford methyl 2,3-*O*-isopropylidene-β-D-*ribo*-hex-5-enofuranoside. The isopropylidene group was hydrolyzed, the hydroxyl groups were blocked with benzoyl groups, and the methoxyl group was replaced with an acetate by acetolysis. The sugar derivative, 1-*O*-acetyl-2,3-di-*O*-benzoyl-5,6-dideoxy-D-*ribo*-hex-5-enofuranose, was condensed with 6-benzamidochloromercuripurine by the titanium tetrachloride method, and the blocking groups were removed with sodium methoxide to afford the desired nucleoside, 9-(5,6-dideoxy-β-D-*ribo*-hex-5-enofuranosyl)adenine. As an aid to NMR clarification of the configuration at the anomeric carbon atom, the 2',3'-*O*-isopropylidene derivative was prepared. D-Talose was converted to methyl 2,3-*O*-isopropylidene-5,6-bis(*O*-methanesulfonyl)-α-D-talofuranoside in several steps without isolation of the intermediates. Sodium iodide treatment of the 5,6-bis(*O*-methanesulfonate) gave methyl 2,3-*O*-isopropylidene-β-L-*ribo*-hex-5-enofuranoside, which was used to prepare 9-(5,6-dideoxy-β-L-*ribo*-hex-5-enofuranosyl)adenine by the same pathway as used to prepare the D form.

This laboratory has been engaged in a study of the chemistry and biological effects of exocyclic unsaturation of nucleosides. In addition to the 4',5' unsaturation found in decoyinine (angustmycin A) type of analogues,[2,3] this laboratory has reported the preparation of several 5',6'-unsaturated hexofuranosyl nucleosides.[4,5] Weak biological activity,

0022-3263/78/1943-2469$01.00/0