

 $C_{33}H_{32}N_2O_{10}\cdot HX$

moiety through a glycosidic link, with the pyrrolopyrrole nitrogen atoms away from the aromatic nucleus and the furan-pyrrolopyrrole system *trans* to the sugar.

The pyrrolopyrrole is planar within ± 0.04 Å. and contains one carbon-carbon double bond. Both nitrogen-to-bridge-carbon distances are equal and shorter than expected for a carbon-nitrogen single bond (1.33 and 1.31 \pm 0.03 Å.). The two secondary hydroxyl groups of the sugar are hydrogen bonded with dioxane molecules of solvation. The latter occupy relatively large cavities in the solid between antibiotic molecules and probably assist in maintaining the orientation of the sugar moiety.

The details of this structure determination will be submitted to *Acta Crystallographica*.

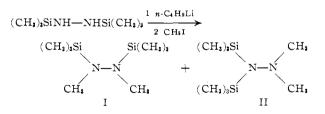
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A Novel Rearrangement of 1,2-Bis(trimethylsilyl)hydrazine

Sir:

In extending the work of Wannagat and co-workers on organosilylhydrazines,¹ we have found a novel rearrangement involving migration of silicon from one nitrogen atom to another. If 1,2-bis(trimethylsilyl)hydrazine is treated with 2 equiv. of *n*-butyllithium in tetrahydrofuran and then with 2 equiv. of methyl iodide, the reaction mixture is found to contain both the expected product, 1,2-bis(trimethylsilyl)1,2-dimethylhydrazine (I), and the rearranged product, 1,1-bis(trimethylsilyl)-2,2-dimethylhydrazine (II).



Pure 1,2-bis(trimethylsilyl)hydrazine, b.p. 147°, n^{25} D 1.4253, d^{24} , 0.834, was prepared by the method of Wannagat and Liehr.^{1a,b,2} This material was shown to

(1) (a) U. Wannagat and W. Liehr, Angew. Chem., **69**, 783 (1957); (b) U. Wannagat and W. Liehr, Z. anorg. allgem. Chem., **297**, 133 (1958); (c) U. Wannagat and H. Niederprum, Angew Chem., **70**, 745 (1958); (d) U. Wannagat and W. Liehr, Z. anorg. allgem. Chem., **299**, 341 (1959); (e) U. Wannagat and H. Niederprum, *ibid.*, **310**, 32 (1961); (f) H. Niederprum and U. Wannagat, *ibid.*, **311**, 270 (1961); (g) U. Wannagat and C. Krueger, and H. Niederprum, *ibid.*, **321**, 198 (1963); (h) U. Wannagat and C. Krueger, *Monatsh. Chem.*, **94**, 63 (1963).

be the 1,2-isomer by reaction with phenyl isocyanate followed by hydrolysis to give hydrazine-N,N'-dicarboxylanilide, m.p. $245-248^{\circ}$, lit. m.p. 245° .^{1h} That it was free of 1,1-isomer was shown by the n.m.r. spectrum which has a single peak in the Si-C-H region at τ 9.92.

In a typical experiment 4.1 g. (0.024 mole) of 1,2bis(trimethylsilyl)hydrazine,² prepared by the method of Wannagat and Liehr, 1a,b was treated with 0.048 mole of *n*-butyllithium in hexane at 0° . After being stirred for about 30 min. to ensure complete reaction, the mixture was chilled to -70° , and 25 ml. of freshly distilled tetrahydrofuran was added, causing the previously white suspension to become light yellow. Methyl iodide (0.48 mole) was then slowly injected. The mixture was then allowed to warm up slowly with stirring, filtered in a drybox, and fractionally distilled yielding 2.8 g. (60%) of pure colorless product, b.p. $67-71^{\circ}$ (17 Torr). *Anal.* Calcd. for $C_8H_{24}Si_2N_2$: C, 46.99; H, 11.83; N, 13.70. Found: C, 47.33; H, 11.97: N, 13.62. The proton n.m.r. spectrum of the product shows two peaks at τ 9.98 and 9.89, assigned to trimethylsilyl protons, and two peaks at τ 7.43 and 7.37, assigned to the methyl protons in the two isomers. Relative peak areas are approximately 3:3: 1:1, respectively, indicating that the two isomers must be present in nearly equal amounts. Partial separation of the mixture could be effected by fractional distillation.

The mixture was solvolyzed with 1-propanol to produce the mixed dimethylhydrazines which were treated with *p*-nitrobenzaldehyde yielding *p*-nitrobenzaldehyde dimethylhydrazone, m.p. 111–112, lit.³ m.p. 111°, infrared spectrum identical with that of authentic *p*-nitrobenzaldehyde dimethylhydrazone. Isolation of this known hydrazone confirms the presence of the rearranged hydrazine in the original reaction mixture.

The rearrangement reported here, though not previously noted, may have occurred in previous reactions of silyl-substituted hydrazines with bases. Thus, in the reaction of 1-phenyl-2-trimethylsilylhydrazine with phenyllithium followed by bromine, a large amount of N-trimethylsilylaniline was observed as a by-product,⁴ perhaps arising via a 1,2-silicon shift of the type described above. Many reactions of lithium derivatives of silvlhydrazines have been reported in which structures of products are assigned without considering the possibility of rearrangement^{1e,g}; some of these structures may now have to be reconsidered in the light of our evidence. At present it is not known whether the rearrangement occurs during or after treatment with n-butyllithium, or even conceivably during the reaction with methyl iodide. Investigations of these possibilities are under way, and studies of the limits and of the reaction in general are planned for the near future.

(3) O. L. Brady and G. P. McHugh, J. Chem. Soc., 121, 1648 (1922).

(4) U. Wannagat and C. Krueger, Z. anorg. allgem. Chem., 326, 288 (1964).

⁽²⁾ The material originally supposed by Wannagat and Liehr^{1a,b} to be 1,2-bis(trimethylsilyl)hydrazine may have been a mixture of the 1,2- and 1,1-isomers (private communication from Professor U. Wannagat). The proportions of the two isomers formed in the reaction of trimethylchlorosilane with hydrazine depends on the reaction conditions in a way not yet fully understood. When present, the 1,1-isomer can easily be detected by n.m.r. spectroscopy (Si-C-H resonance at τ 9.99).

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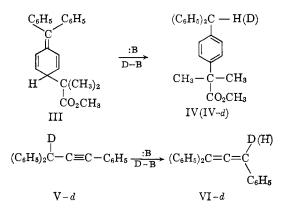
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Base-Catalyzed Intramolecular 1,3- and 1,5-Proton Transfers

Sir:

Since the report of the first base-catalyzed intramolecular 1,3-proton transfer,¹ enough other examples² have appeared in the literature to suggest that the phenomena might be rather general. Support for this view is found in a number of examples of enzymecatalyzed intramolecular proton transfers that have been observed.3



molecular proton transfers which lend substantial

in a variety of deuterated solvents, gave IV6 with

intramolecularity that varied from 17 to 98% (Table

Compound III,⁵ when treated with various bases

support to these "conducted tour" mechanisms.

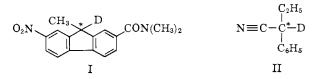
TABLE I

Intramolecularity in Base-Catalyzed Proton (Deuteron) Transfers in Triene III to Give Triarylmethane IV and in D----

Deuterated Acetylene (V) to Give Allene VI a					
Run no.	Compd.	Solvent ^b	Base	<i>T</i> , °C.	% intramolecular
1	III	$(CH_2OD)_2$	$DOCH_2CH_2OK$	55	17
2	III	$(CH_2)_4O-10\% D_2O$	DONa	25	34
3	III	$(CD_3)_2SO-10\%$ CH ₃ OD	CH3OK	25	40
4	III	CH₃OD	CH ₃ ONa	25	47
5	III	t-BuOD	t-BuOK	25	50
6	III	$(C_2H_5)_3COD$	$(C_3H_7)_3N$	75	98
7	III	$(C_2H_5)_3COD^c$	(C ₃ H;) ₃ N	75	97
8	III	$(C_2H_5)_3COD^d$	(C ₃ H ₇) ₃ N	75	98
9	V	t-BuOD	t-BuOK	30	22 ± 3
10	V - d^e	CH₃OH	CH3OK	30	19
11	$V \cdot d^e$	$(CH_3)_2$ SO-1.6 M t-BuOH	$N(CH_2CH_2)_3N$	30	88
12	V - d^e	$(CH_3)_2SO-3.9 M CH_3OH$	$N(CH_2CH_2)_3N$	30	88
13	$V-d^{e}$	$(CH_3)_2SO-3.9 M CH_3OH'$	$N(CH_2CH_2)_3N$	30	85
14	$V \cdot d^e$	$(CH_3)_2SO-3.9 M CH_3OH^f$	$(CH_2)_5 NH$	30	58

^a All deuterium analyses were made by combustion and falling drop method (J. Nemeth). Products once formed underwent little if any exchange under conditions of their formation. ^b Solvents 97-100% deuterated where deuterium is indicated. ^c Solution was 0.1 M in $(C_4H_5)_4NI$. d Solution was 0.1 M in $(C_3H_7)_3NDI$. e 95% of 1 atom of deuterium. Results were corrected accordingly. [/] Solution was 0.14 M in N(CH₂CH₂)₂NHI.

In studies of the stereochemistry of base-catalyzed hydrogen-deuterium exchange of I and II, examples of intramolecular racemization (isoracemization) were interpreted as occurring by a series of intramolecular proton transfers (conducted tour mechanism).⁴ Some of the steps involved 1,6-proton transfers across an aromatic system (I), others 1,3-proton transfers from carbon α to a cyano group to nitrogen and back to



We have now observed examples of intracarbon.

(3) (a) F. S. Kawahara and P. Talalay, J. Biol. Chem., 235, PC 1 (1960); (b) B. W. Agranoff, H. Eggerer, U. Henning, and F. Lynen, ibid., 235, 326

(1960); (c) H. C. Rilling and M. J. Coon, ibid., 235, 3087 (1960).

(4) 1), J. Cram and L. Gosser, J. Am. Chem. Soc., 86, 2950 (1964).

I). This rearrangement involves proton transfer across the face of a benzene ring. Compound V (deuterated) under similar conditions with base in protonated solvents gave VI with intramolecularity that varied between about 20 and 88% (Table I).

The isomerization of triene III to aryl compound IV can be visualized as occurring by one 1,5-rearrangement, or by two successive 1,3-rearrangements. Evidence that the latter type of mechanism makes little, if any, contribution is shown by the fact that no deuterium could be detected in the aromatic rings of IV (combination of n.m.r. and combustion techniques) produced in those runs which gave low intramolecularity (1-5). Had intermediates such as VII-d intervened, some deuterium should have been incorporated into the ortho position of the para-substituted ring of IV.

These rearrangements are interpreted as occurring largely through ion-pair intermediates whose carbanion is hydrogen bonded to the molecule of oxygen or nitrogen acid generated by proton (deuterium) abstrac-

⁽¹⁾ D. J. Cram and R. T. Uyeda, J. Am. Chem. Soc., 84, 4358 (1962). (2) (a) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, ibid., 85, 2115 (1963); (b) R. B. Bates, R. H. Carnighan, and C. E. Staples, ibid., 85, 3032 (1963); (c) W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963); (d) G. Bergsen and A. M. Weidler, Acta Chem. Scand., 17, 862, 1798 (1963); (e) G. Bergsen, ibid., 17, 2691 (1963); (f) D. J. Cram and R. T. Uyeda, J. Am. Chem. Soc., in press.

⁽⁵⁾ R. Heck, P. S. Magee, and S. Winstein, Tetrahedron Letters, 30, 2033 (1964).

⁽⁶⁾ All new compounds used in this investigation gave carbon and hydrogen analysis within 0.3% of theory. All old compounds gave physical properties which corresponded to literature values.