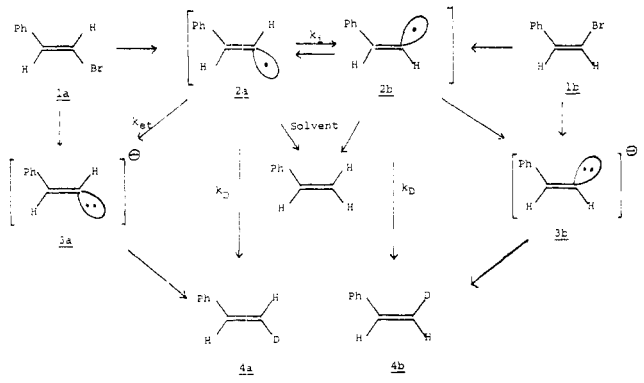
Scheme I



mentally,[6] again in accordance with the calculated inversion barrier of 31.1 kcal/mol.[5] On the basis of the reasonable assumption that the rate of inversion of configuration of the β-styrenyl radical would be similar to that established for the vinyl radical ($k_i \simeq 10^{8-10}$ s^{-1}),[7] it is expected that the reduction of β-bromostyrene (1) by $LiAlD_4$ would result in a loss of stereochemistry, if such radicals are involved as intermediates.

The readily available *trans*- and *cis*-β-bromostyrenes (**1a** and **1b**) were reduced with $LiAlD_4$ under a variety of conditions, and the results are summarized in Table I. Styrene was obtained as the major product in all of the runs along with the starting material and some polymeric products. The percent of deuterium incorporation in sytrene (d_1/d_0) was determined by mass spectral analysis, and the rations of *trans*- and *cis*-β-deuteriostyrenes (**4a**/**4b**) were measured by NMR spectral analysis in the region of δ 5.0–6.0.[8]

The data clearly show a number of useful features. First, the reduction at room temperature (runs 1–3 and 9–10) proceeds with a virtually complete loss of stereochemistry regardless of the substrate geometry (trans or cis) or choice of the solvent (ether or THF). In a striking contrast, reduction at refluxing THF temperature (runs 4 and 11) proceeds with a predominant retention of the configuration. It is also interesting to compare these stereochemical results with $LiAlD_4$ with those of $(n\text{-Bu})_3SnD$ in refluxing benzene and Zn–Cu in refluxing EtOD—conditions known to proceed via radical intermediates[9] and electron-transfer processes,[10] respectively. Second, a significant amount of nonlabeled styrene (d_0) was produced in all the runs, indicating that the intermediate is capable of abstracting hydrogen from both the metal hydride and the solvents. The control experiments involving the substrate reduction with $LiAlH_4$ followed by D_2O workup (runs 5 and 12) demonstrate that the reduction was complete before the aqueous workup.

Although intervention of a β-styrenyl carbonium ion could result in the loss of stereochemistry, such a highly energetic species is very unlikely to be produced under the reaction conditions.[11] Another possible cause for the loss of stereochemistry, namely, elimination of HBr followed by reduction with $LiAlD_4$, could be readily excluded by the following control experiments. Phenylacetylene was never detected during the course of reduction by a careful GC analysis, nor was it reduced to styrene under the identical reaction conditions. It was also observed that the starting material did not undergo geometrical isomerization prior to the reduction. Therefore, it appears that the data obtained from $LiAlD_4$ reductions of **1a** and **1b** at room temperature may be best accommodated by a mechanistic picture involving the two rapidly interconverting radicals **2a** and **2b** as depicted Scheme I. The predominant retention of the stereochemistry in the $LiAlD_4$ reduction of **1a** and **1b** at refluxing THF temperature is unexpected. Although these results can be rationalized by the radical mechanistic scheme, with the assumption that the k_{et} step is markedly temperature dependent, it appears possible that entirely different reaction pathways, e.g., S_N2 displacement on bromine resulting in carbanion formation or stereospecific syn addition of $LiAlD_4$ followed by anti elimination of $LiAlD_3Br$ etc., might be operating under the elevated temperature conditions. In summary, the evidence seems to suggest the involvement of a radical mechanistic pathway in the metal hydride reduction of vinyl halides under certain conditions.

Experimental Section

Lithium aluminum hydride and deuteride were purchased from Ventron Corp. (Alfa Division). The NMR spectra were obtained on a Varian Associates Model T-60 or CFT-20 with Me_4Si as internal standard. Mass spectral analyses were done on a Hewlett-Packard GC/MS system, Model 5982-A. GC analyses were performed with an Antek Instruments Model 300 and a Varian Aerograph Model 2700 by using the following columns: 5 ft, 10% OV-101; 5 ft, 10% FFAP on Anakrom-SD, 60/70 mesh. The NMR measurement of β-deuteriostyrenes was carried out according to the established literature method.[8]

***trans*-β-Bromostyrene (1a)** was purchased from Aldrich Chemical Co. and purified according to a literature procedure,[8] and was at least 92% isomerically pure by GC analysis (FFAP column).

***cis*-β-Bromostyrene (1b)** was prepared from *trans*-cinnamic acid according to a literature procedure,[12] and was at least 90% isomerically pure by GC analysis (FFAP column).

Acknowledgment. I am very grateful to the Robert A. Welch Foundation (Grant A-752) for the financial support and to Paul Fagerness for assistance in NMR measurement.

Registry No. **1a**, 588-72-7; **1b**, 588-73-8; $LiAlH_4$, 16853-85-3.

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p 130.
(7) L. A. Singer in "Selective Organic Transformations", Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1972, p 239; O. Simamura, *Top. Stereochem.*, **4**, 1 (1969); M. Tamura and J. Kochi, *J. Am. Chem. Soc.*, **93**, 1487 (1971); G. M. Whitesides and C. P. Casey, *ibid.*, **88**, 4541 (1966); E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 764 (1964).
(8) T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Am. Chem. Soc.*, **86**, 4670 (1964).
(9) H. G. Kuivila, *Acc. Chem. Res.*, 1, 299 (1968); H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).
(10) R. M. Blankenship, K. A. Burdett, and J. S. Swenton, *J. Org. Chem.*, **39**, 2300 (1974).
(11) P. J. Stang, *Acc. Chem. Res.*, **11**, 107 (1978).
(12) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953).

Unequivocal Assignment of the Skeletal Structure of the Guanine–Glyoxal Adduct

Anthony W. Czarnik and Nelson J. Leonard*

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

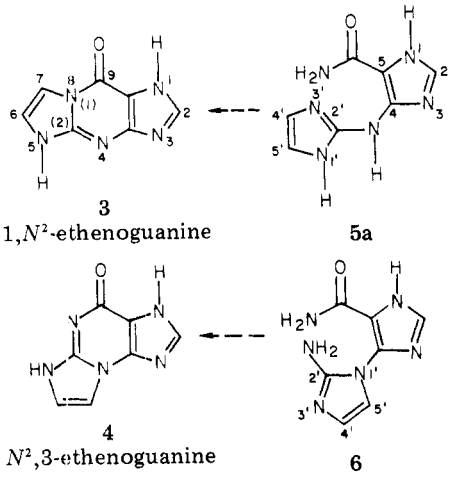
Received January 31, 1980

The reaction of guanine and its derivatives with various aldehydes has been shown to be useful in the base-selective modification of both DNA[1,2] and RNA.[2,3] Monocarbonyl

(1) Reiss, U.; Tappel, A. L.; Chio, K. S. *Biochem. Biophys. Res. Commun.* **1972**, *48*, 921.

0022-3263/80/1945-3514$01.00/0

Scheme I



3
1,N^2-ethenoguanine

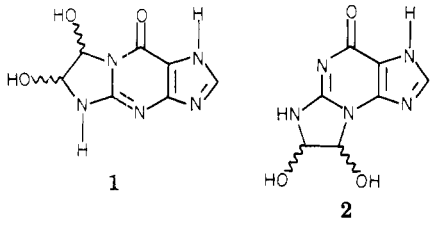
5a

4
N^2,3-ethenoguanine

6

aldehydes (formaldehyde,[4] glycidaldehyde,[5] chloroacetaldehyde[6]), dicarbonyl aldehydes (glyoxal,[3,7] 3-ethoxy-2-oxobutyraldehyde (Kethoxal),[3,8,9] pyruvaldehyde,[9] substituted[10] and unsubstituted[1] malondialdehydes), and ninhydrin[11] form covalent adducts with guanine derivatives, often in preference to the other usual nucleic acid bases, under defined conditions.[3]

Staehelin[3] first showed that glyoxal formed an adduct with guanosine 5′-monophosphate, the structure of which was not determined. The reactions of guanosine[11] and guanine[9] with glyoxal were later reported in separate accounts. On the basis of NMR spectra and degradation results, the site of reaction was found to include N-2 and one endocyclic nitrogen of the base, leading to the logical assignment of the "linear" isomer **1** as the structure of the

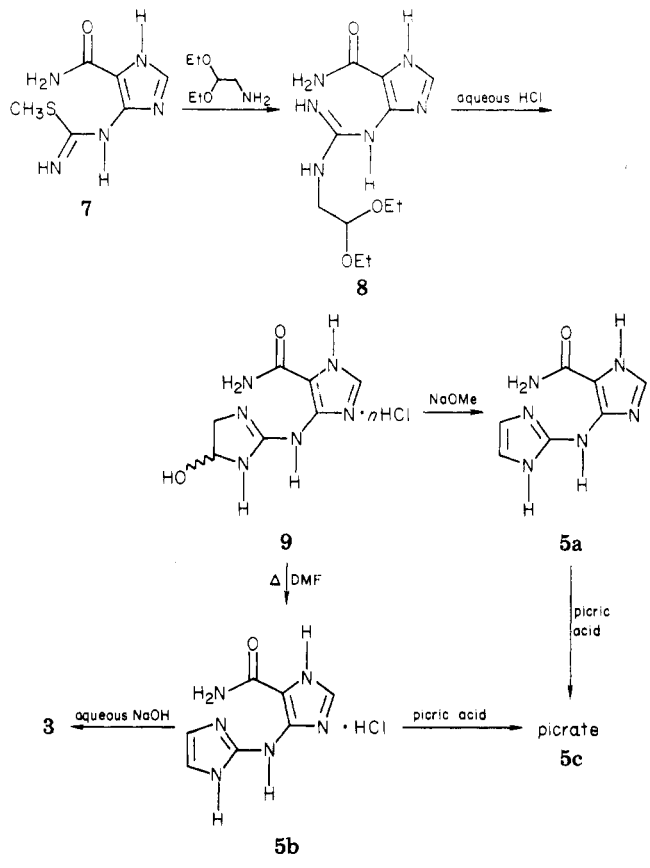


1

2

adduct. However, the possibility that the guanine–glyoxal adduct had a different skeletal structure, i.e., that of the "bent" isomer **2**, was apparently not explored. Subsequent chemical transformations have not distinguished between these isomers, and structure assignments for related systems to date have relied on the results of the initial study. For example, we recently reported that the guanine–glyoxal adduct can be converted readily in one step to the corresponding etheno derivative which, on the basis of UV and NMR spectral similarities to model systems, was assigned the structure of the 1,N^2 isomer (**3**).[6] This same compound is formed upon reaction of guanosine with chloroacetaldehyde at pH 6.5 followed by acid hydrolysis to effect

Scheme II



7

8

9

5a

5b

picrate
5c

deribosidation.[6] Although all of the reports thus far have been internally consistent, we considered it desirable to confirm the linear structure assignments of **1** and **3**, and thus rule out **2** and **4**, by independent and unequivocal means.

We now report an unequivocal synthesis of 1,N^2-ethenoguanine that provides unambiguous assignment of the "linear" tricyclic structure **1** to the guanine–glyoxal adduct and thus of similar linear skeletal structures to all related compounds. If the 8,9 bond is formed in the final step of the synthesis of 1,N^2-ethenoguanine (Scheme I), a potential precursor to the desired final product is the bisimidazole **5a**. This compound would be readily distinguishable from its structural isomer **6** by NMR, owing to the expected magnetic equivalence of both the 4′ and 5′ imidazole carbons and protons in compound **5a** but not in **6**. The equivalence in the former is due to the rapid exchange of tautomeric forms and rapid rotation about the exocyclic C–N bond at room temperature.[12]

Our synthesis began with 4-(*S*-methylisothiocarbamoyl)amino-5-imidazolecarboxamide (**7**), which is readily available[14] from 4-amino-5-imidazolecarboxamide. The conversion of this isothiourea (**7**) to the corresponding guanidino compound **8** was accomplished in 69% yield, based on unrecovered starting material (Scheme II). Competing reactions leading to the decomposition of compound **8** prevented improvement in its yield when the reaction time was extended beyond 3 h. Treatment of the acetal **8** with aqueous acid at room temperature afforded the hydroxyimidazoline derivative **9** in quantitative yield as judged by ^{1}H and ^{13}C NMR spectra. The choice be-

(2) Fraenkel-Conrat, H. *Biochim. Biophys. Acta* **1954**, *15*, 307.
(3) Staehelin, M. *Biochim. Biophys. Acta* **1959**, *31*, 448.
(4) Scheit, K. H. *Tetrahedron Lett.* **1965**, 1031.
(5) Goldschmidt, B. M.; Blazej, T. P.; Van Duuren, B. L. *Tetrahedron Lett.* **1968**, 1583.
(6) Sattsangi, P. D.; Leonard, N. J.; Frihart, C. R. *J. Org. Chem.* **1977**, *42*, 3292.
(7) Whitfeld, P. R.; Witzel, H. *Biochim. Biophys. Acta* **1963**, *72*, 338.
(8) Litt, M.; Hancock, V. *Biochemistry* **1967**, *6*, 1848.
(9) Shapiro, R.; Cohen, B. I.; Shiuey, S.-J.; Maurer, H. *Biochemistry* **1969**, *8*, 238.
(10) Moschel, R. C.; Leonard, N. J. *J. Org. Chem.* **1976**, *41*, 294.
(11) Shapiro, R.; Hachmann, J. *Biochemistry* **1966**, *5*, 2799.
(12) Batterham, T. J. "NMR Spectra of Simple Heterocycles"; Wiley-Interscience: New York, 1973; p 215.
(13) Albert, A. *Adv. Heterocycl. Chem.* **1976**, *20*, 117.
(14) Yamazaki, A.; Kumashiro, I.; Takenishi, T. *J. Org. Chem.* **1967**, *32*, 1825.

tween the two possible isomeric hydroxyimidazolines (ignoring tautomeric forms) could not be made until subsequent conversion to the corresponding imidazole was effected. Assignment as the ring-closed compound **9** rather than the isomeric open-chain aldehyde rests on the ^1H NMR spectrum in which we observed (1) the absence of a signal characteristic of aldehyde proton resonance (δ 9.5–10.0) and (2) an ABX splitting pattern that would not be expected for the aldehyde. Many other examples of such covalently hydrated heterocycles are now known, and the topic has been recently reviewed.[13]

Dehydration of the hydroxyimidazoline **9** was accomplished either by heating or by neutralization with sodium methoxide. The bisimidazole **5a** or hydrochloride **5b** thus obtained decomposed thermally or in the presence of water, making it difficult to obtain a pure sample of the free base or hydrochloride salt; however, an identical picrate (**5c**) was readily obtained from either source. The facile conversions of **5a** and **5b** to **5c** confirm the equivalence of the dehydration methods.

The ^1H NMR spectra of compounds **5b** and **5c** in D_2O, $(CD_3)_2SO$, or pyridine-d_5 showed only a single sharp resonance for the 4′,5′-imidazole protons, demonstrating their magnetic equivalence. Similarly, a single resonance was observed for the 4′,5′-imidazole carbons of **5b** in the ^{13}C NMR spectrum. These findings clearly affirm the structure assignment of the bisimidazole as **5a** rather than **6**.

Base-catalyzed ring closure of **5b** to 1,N^2-ethenoguanine (**3**) was accomplished in good yield with aqueous NaOH under nitrogen. A sample of the guanine–glyoxal adduct[9] was converted to the corresponding ethenoguanine upon treatment with HI as reported from this laboratory.[6] This latter compound was identical in all respects with the 1,N^2-ethenoguanine prepared in our synthesis, and both samples were easily distinguishable from the isomeric N^2,3-ethenoguanine (**4**).[6] The direct comparison provides confirmation of the "linear" skeletal structure that has been assumed, without unequivocal evidence heretofore, for the guanine–glyoxal adduct and for the entire family of related compounds.

Experimental Section

Melting points were determined on a Büchi capillary melting point apparatus and are uncorrected. ^1H nuclear magnetic resonance spectra were recorded on a Varian EM-390 or HR-220 spectrometer, using tetramethylsilane with deuterated organic solvents or acetone (δ 2.07) with D_2O solutions as an internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-60 Fourier transform instrument operating at 15.03 MHz and are reported in parts per million, using tetramethylsilane with deuterated organic solvents or dioxane (δ 66.58) with D_2O solutions as an internal standard. Mass spectra were run on a Varian MAT CH-5 low-resolution or a Varian MAT-731 high-resolution spectrometer coupled with a 620i computer and a Statos recorder. Ultraviolet absorption spectra were obtained on a Beckman Acta MVI spectrophotometer.

Thin-layer chromatography (TLC) was performed on Merck silica gel f-254 plates (thickness, 0.25 mm); the solvent systems employed were the following: solvent A, 1-butanol–glacial acetic acid–H_2O (4:1:1); solvent B, isobutyric acid–0.5 M NH_4OH (5:3). Brinkmann 0.05- to 0.2-mm silica gel was used for column chromatography on silica. *N,N*-Dimethylformamide (DMF) was purified before use by stirring over KOH pellets for several hours followed by distillation from BaO. Methanol and ethanol used were of anhydrous grade. Microanalyses were performed either by Mr. Josef Nemeth and associates or by Midwest Microlab, Ltd., Indianapolis, IN.

4-[*N*-(2,2-Diethoxyethyl)]guanidino-5-imidazolecarboxamide (8). To a solution of the isothiourea **7**[14] (7.50 g, 37 mmol) in 250 mL of dry DMF was added freshly distilled aminoacetaldehyde diethyl acetal[15] (11.0 g, 83 mmol), and the resulting solution was heated at reflux with stirring and with the exclusion of moisture for 3 h. The reddish-orange solution was evaporated in vacuo, and the solid residue was applied to a 48 × 4 cm column of silica gel. The column was eluted with 1000 mL of 5% MeOH in CH_2Cl_2 to remove starting material (**7**), followed by 10% MeOH in CH_2Cl_2 to elute the product. The UV-absorbing fractions were checked by TLC in solvent A, and appropriate fractions were pooled and evaporated to dryness to yield starting material (3.08 g, 41%) and a colorless solid (4.34 g, 69% based on unrecovered **7**). An analytical sample was obtained by repeated recrystallization from EtOAc: mp 147–148 °C; R_f 0.45 (solvent A); ^1H NMR ($(CD_3)_2SO$) δ 1.05 (t, 6, J = 7.0 Hz, CH_3), 3.10 (dd, 2, NCH_2, coalesces to doublet, J = 6.0 Hz, with D_2O), 3.35 (m, 4, OCH_2), 4.40 (t, 1, J = 6.0 Hz, aliphatic CH), 6.65 (br s, 1, amide NH exchangeable with D_2O), 6.85 (br s, 1, amide NH exchangeable with D_2O), 7.05 (s, 1, CH), 7.95 (br s, 1, NH exchangeable with D_2O); ^{13}C NMR ($(CD_3)_2SO$) δ 15.26 (CH_3), 43.54 (NCH_2), 61.69 (OCH_2), 100.44 (OCH), 111.01 (=CCONH$_2$), 132.63 (N=CHNH), 150.78 (=CNHC(=NH)NH), 154.55 (NC(=NH)N), 162.57 (C(=O)NH$_2$); mass spectrum, m/e 284 (M^+).

Anal. Calcd for $C_{11}H_{20}N_6O_3$: C, 46.47; H, 7.09; N, 29.56. Found: C, 46.61; H, 6.94; N, 29.30.

4-(4′-Hydroxyimidazolin-2′-yl)amino-5-imidazolecarboxamide Hydrochloride (9). A solution of the substituted guanidinoimidazole **8** (1.00 g, 3.5 mmol) in 100 mL of 6 M hydrochloric acid was allowed to stand at 20 °C for 10 min. The solution was evaporated to dryness in vacuo and coevaporated with 50 mL of EtOH to obtain a colorless solid which was used directly in the next stage: mp 140–160 °C dec; R_f 0.39 (solvent A); ^1H NMR (D_2O) δ 3.60 (dd, 1, J = 2.7, 12 Hz, aliphatic CH syn to OH), 4.05 (dd, 1, J = 7.2, 12 Hz, aliphatic CH anti to OH), 5.85 (dd, 1, J = 2.7, 7.2 Hz, aliphatic OCH), 8.85 (s, 1, Ar CH); ^{13}C NMR (D_2O) δ 49.80 (CH_2), 66.58 (dioxane), 85.08 (OCH), 124.02, 124.56, 135.42 (NCH), 156.77, 159.08 (C(=O)NH$_2$); field-desorption mass spectrum (15 mA), m/e 284 (starting material), 211 (MH^+), 210 (M^+), 192 ($M^+ - H_2O$).

4-(Imidazol-2′-yl)-5-imidazolecarboxamide Hydrochloride (5b). A solution of the crude hydroxyimidazoline hydrochloride (**9**) in 150 mL of dry DMF was heated rapidly but momentarily to incipient reflux under dry N_2. The solution was reduced to a small volume in vacuo, then 30 mL of absolute EtOH was added, and the mixture was swirled to homogeneity. Upon dropwise addition of petroleum ether with magnetic stirring a precipitate formed which was collected by filtration and dried under high vacuum to yield 699 mg (87%, based on **8**) of an off-white solid: mp >300 °C; R_f 0.39 (solvent A); ^1H NMR ($(CD_3)_2SO$) δ 7.10 (s, 2, equivalent CH's), 7.80 (br s, 2, NH exchangeable with D_2O), 7.90 (s, 1, Ar CH); ^{13}C NMR ($(CD_3)_2SO$) δ 106.67 (=CCONH$_2$), 114.12 (equivalent C's), 133.69 (NCH), 141.34, 142.02, 161.95 (C(=O)NH$_2$).

4-(Imidazol-2′-yl)amino-5-imidazolecarboxamide Picrate (5c). A solution of the hydroxyimidazoline hydrochloride **9**, prepared from 200 mg (0.70 mmol) of **8**, in 25 mL of absolute MeOH was adjusted to pH 10 (H_2O-moistened pH paper) with sodium methoxide in MeOH. The solution was neutralized with glacial acetic acid, and then a 10% solution of picric acid in absolute MeOH (2 mL) was added. The resulting mixture was allowed to stand at room temperature for 30 min, and the solid was collected by filtration. Washing with hot 1-propanol followed by drying under vacuum gave 251 mg (85%) of a yellow solid: mp 274–275 °C dec; ^1H NMR ($(CD_3)_2SO$) δ 6.75 (s, 2, equivalent CH's), 7.15 (br s, 1, NH exchangeable with D_2O), 7.50 (s, 1, imidazole CH), 8.20 (s, 2, picrate CH's).

Anal. Calcd for $C_{13}H_{11}N_9O_8$: C, 37.06; H, 2.64; N, 29.93. Found: C, 36.75; H, 2.64; N, 30.11.

A sample of the **free base (5a)** was prepared as follows: After neutralization with glacial acetic acid in the procedure described above, the solution was evaporated to dryness. The white residue was extracted with hot 1-propanol and the solution was evaporated to dryness in vacuo. The discolored residue was recrystallized from absolute EtOH to give a solid: mp 215–217 °C dec (darkening begins at 195 °C); mass spectrum, m/e 192 (M^+), 175 ($M^+ - NH_3$, base peak); high-resolution mass spectrum, exact mass

(15) Obtained from Aldrich Chemical Co., Milwaukee, WI.

calcd for $C_7H_8N_6O$ 192.0759, obsd 192.0753.

Conversion of 5b to 5c. A solution of 25 mg (0.11 mmol) of **5b** in 8 mL absolute MeOH was treated with 0.5 mL of a 10% solution of picric acid in MeOH, and the resulting mixture was allowed to stand at room temperature for 30 min. The precipitate was filtered and dried under vacuum to afford 39 mg (85%) of a yellow solid which was shown to be identical with **5c**, prepared as described above, by TLC and "mixed" ^{1}H NMR.

1,N^2-Ethenoguanine (5,9-Dihydro-9-oxoimidazo[1,2-*a*]-purine) (3). A solution of the bisimidazole hydrochloride **5b** (250 mg, 1.1 mmol) in 25 mL of 1 M NaOH was heated to gentle reflux with stirring under N_2 for 1 h. The solution was adjusted to pH 7 with glacial acetic acid, and the resulting mixture was cooled at 5 °C for 1 h. The precipitate was collected by filtration, washed with hot 1-propanol, and dried overnight under vacuum at 120 °C to yield 160 mg (84% based on unhydrated free base) of an off-white solid: mp >300 °C. This material was compared with an authentic sample of the product obtained by HI reduction of the guanine–glyoxal adduct[6] and was found to be identical by TLC in two systems (R_f 0.47, solvent A; 0.68, solvent B), mass spectrometry, UV, and "mixed" ^{1}H NMR (HI salts).

Acknowledgment. This work was supported by Research Grant GM 05829 from the National Institutes of Health, U.S. Public Health Service. High-resolution and field-desorption mass spectral data were obtained in part under a grant from the National Cancer Institute (CA 11388), National Institutes of Health. We thank B. W. Fisher for his technical assistance and Dr. G. E. Keyser and Dr. J. D. Bryant for their valuable suggestions during the course of this work.

Registry No. 3, 56287-13-9; **5a**, 73971-13-8; **5b**, 73971-14-9; **5c**, 73971-15-0; 7, 10333-88-7; 8, 73971-16-1; 9, 73971-17-2; aminoacetaldehyde diethyl acetal, 645-36-3; picric acid, 88-89-1.

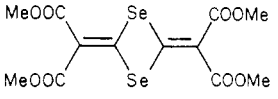
2,2,4,4-Tetrakis(trifluoromethyl)- and 2,4-Bis(hexafluoroisopropylidene)-1,3-diselenetane

Maynard S. Raasch

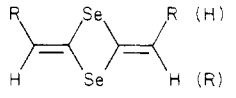
Central Research and Development Department,[1] Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received March 13, 1980

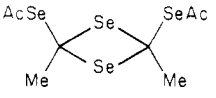
The nine known 1,3-diselenetanes (1,3-diselenacyclobutanes) have been synthesized by a variety of approaches.[2] Polymerization of selenocarbonyl fluoride followed by cracking of the polymer yields tetrafluoro-1,3-diselenetane.[3] Treatment of this compound with boron trichloride and with boron tribromide provides tetrachloro- and tetrabromo-1,3-diselenetane, respectively.[3b] Tetraacetyl-1,3-diselenetane has been made by the reaction of acetylacetone with selenium tetrachloride,[4] and 1 results from the reaction of carbon diselenide with the anion of dimethyl malonate.[5] Thermal decomposition of 1,2,3-selenadiazoles produces **2**.[6] Compound **3** is obtained from acetyl chloride and hydrogen selenide in the presence of aluminum chloride.[7]



1

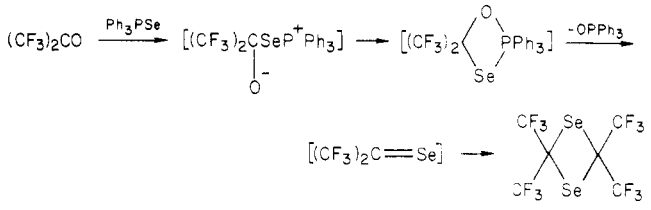


2, R = H, Me, *t*-Bu



3

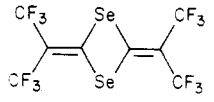
Tetrakis(trifluoromethyl)-1,3-diselenetane (**4**) has now been readily made in 73% yield by heating hexafluoroacetone and triphenylphosphine selenide at 150 °C for 5 h. Presumably, the oxygen–selenium exchange takes place through a cyclic four-membered intermediate. The mass spectrum of **4** is in agreement with the structure and provides no evidence indicative of the 1,2-diselenetane isomer.



4

This diselenetane was reported[8] in 6.4% yield as one of the products from the reaction of hexafluoropropene with selenium in the presence of antimony pentafluoride, but no melting point or characterization other than the mass spectrum was given.

Similarly, bis(trifluoromethyl)ketene and triphenylphosphine selenide provide 2,4-bis(hexafluoroisopropylidene)-1,3-diselenetane **5** in 16% yield. The ^{19}F



5

NMR singlet for **5** eliminates the isomeric 1,2-diselenetane structure. This synthesis is less successful than the reaction of the ketene with triphenylphosphine sulfide which gives the sulfur analogue of **5** in 60% yield.[9]

Experimental Section

The ^{19}F NMR spectra were measured with a Varian XL-100 instrument with CCl_3F as internal standard. A Du Pont 900 differential thermal analyzer was used for thermal analysis.

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-diselenetane (4). Triphenylphosphine selenide[10] was made by heating a stirred mixture of triphenylphosphine and selenium powder in a flask in an oil bath at 190 °C for 2.5 h and recrystallizing the product from ethanol, mp 188–189 °C.

(1) Contribution no. 2764.

(2) For a discussion of compounds that have been erroneously referred to in some books and reviews as 1,3-diselenetanes, see: Margolis, D. S.; Pitman, R. W. *J. Chem. Soc.* **1957**, 799–805.

(3) (a) Haas, A.; Koch, B.; Welcman, N. *Chem.-Ztg.* **1974**, *98*, 511–512. (b) Haas, A. *Chem. Scr.* **1975**, *8A*, 75–78. Haas, A.; Koch, B.; Welcman, N. *Z. Anorg. Allg. Chem.* **1976**, *427*, 114–122. (c) Wehrung, T.; Oberhammer, H.; Haas, A.; Koch, B.; Welcman, N. *J. Mol. Struct.* **1976**, *35*, 253–262.

(4) Dewar, D. H.; Fergusson, J. E.; Hentschel, C. J.; Wilkins, C. J.; Williams, P. P. *J. Chem. Soc.* **1964**, 688–691.

(5) Jensen, K. A.; Henriksen, L. *Acta Chem. Scand.* **1970**, *24*, 3213–3229.

(6) Holm, A.; Berg, C.; Bjerre, C.; Bak, B.; Svanholt, H. *J. Chem. Soc., Chem. Commun.* **1979**, 99–100.

(7) Olsson, K.; Almqvist, S.-O. *Acta Chem. Scand.* **1969**, *23*, 3271–3272.

(8) Kopaevich, Y. L.; Belen'kii, G. G.; Mysov, E. I.; German, L. S.; Knunyants, I. L. *Zh. Vses. Khim. Ova.* **1972**, *17*, 226–227; *Chem. Abstr.* **1972**, *77*, 101427.

(9) Raasch, M. S. *J. Org. Chem.* **1970**, *35*, 3470–3483.

(10) Michaelis, A.; Soden, H. v. *Justus Liebigs Ann. Chem.* **1885**, *229*, 295–334. Nicpon, P., Meek, D. W. *Inorg. Synth.* **1967**, *10*, 157–159. This reagent can be purchased.

0022-3263/80/1945-3517$01.00/0