Purine N oxides. XLVIII. l hydroxyguanine

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · AUGUST 1973

Impact Factor: 4.72 · DOI: 10.1021/jo00957a026

Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 71.98; H, 7.53.

15-Oxaestrone (1).—A solution of 12 g of **34**, 250 ml of dioxane, and 20 ml of an 8% aqueous sulfuric acid solution was stirred and refluxed for 4 hr. The solution was cooled and poured into 2 l. of ice water, and the precipitate was filtered. The product was washed thoroughly with water and air dried. The crude material was then dissolved in a minimum of 1:1 methylene chloride–tetrahydrofuran solution, dried ($MgSO_4$), and heated with charcoal. The mixture was filtered and the solvent removed under reduced pressure. The resulting residue was triturated with ether to give 9.2 g of crude product. Crystallization from methanol afforded two crops of product: 7.0 g, mp 254–256°; and 1.4 g, mp 252–254°. The total yield of 1 was 8.4 g (81%). Crystallization from methanol of the first crop afforded an analytical sample, mp 255–256°, $[\alpha]^{15}D$ +108.45° (*c* 0.8760, $CHCl_3$).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.28; H, 7.84.

Acknowledgments.—The authors wish to thank Dr. R. W. Kierstead for his interest and stimulating discussions of this work. We also wish to thank Dr. T. Williams and Dr. W. Benz for the nmr and mass spectra, respectively, as well as Dr. F. Scheidl for the microanalyses.

Registry No.—**1**, 40715-31-9; **3**, 6217-96-5; **4a**, 6217-97-6; **4b**, 6217-98-7; **5b**, 19018-70-3; **6**, 40715-35-3; **7**, 19018-71-4; **8a**, 40715-37-5; **8b**, 26362-62-9; **9**, 21491-12-3; **10b**, 40715-40-0; **10c**, 40715-41-1; **11**, 40715-42-2; **14**, 40715-43-3; **23**, 40715-44-4; **24**, 40715-45-5; **25**, 40715-46-6; **26**, 40715-47-7; **27**, 40715-48-8; **28**, 40715-49-9; **29**, 40830-80-6; **29** 3β-acetoxy derivative, 40715-51-3; **30**, 40715-52-4; **31**, 40715-53-5; **32**, 40715-54-6; **33**, 40715-55-7; **34**, 40715-56-8; *m*-chloroperbenzoic acid, 937-14-4; lead tetraacetate, 546-67-8.

Notes

Purine *N*-Oxides. XLVIII. 1-Hydroxyguanine[1]

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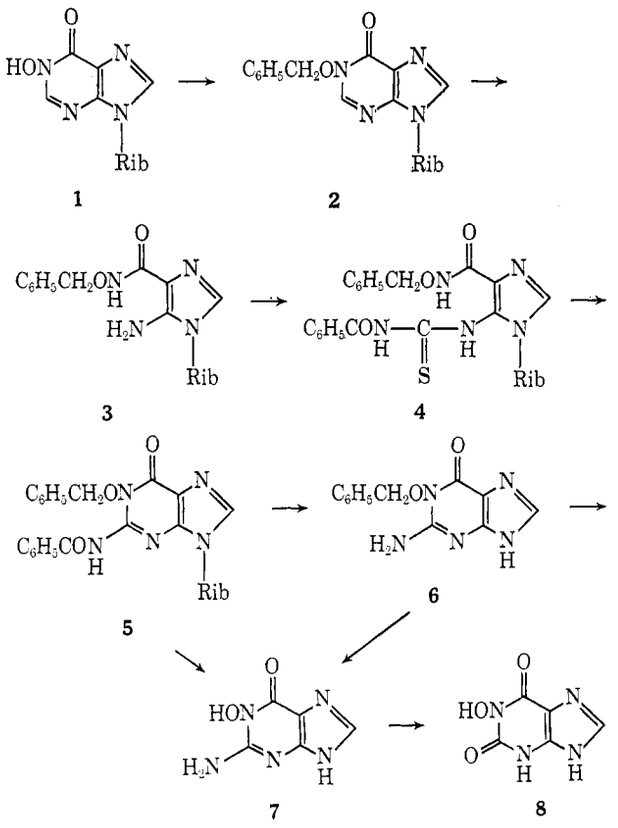
Received December 20, 1972

The 1- and 3-*N*-oxide isomers of adenine,[2,3] hypoxanthine,[3,4] and xanthine[5,6] are available, but only the 3 isomer of guanine.[6] By an adaptation of the synthetic route which led *via* substituted imidazoles to a series of 9-hydroxypurines,[7,8] it has now been possible to obtain 1-hydroxyguanine. 1-Hydroxyinosine (**1**), obtained by the nitrosation of adenosine 1-*N*-oxide,[9a] was converted to 1-benzyloxyinosine[9a] (**2**) by reaction with benzyl bromide in DMF in the presence of K_2CO_3. By refluxing **2** in ethanol containing 0.2 volumes of 6 *N* NaOH, the pyrimidine ring was opened to yield 5-amino-1-β-D-ribofuranosylimidazole-4-*N*-benzyloxycarboxamide (**3**). Refluxing **3** with 1 equiv of benzoyl isothiocyanate in acetone yielded 5-(*N'*-benzoylthiocarbamoyl)amino-1-β-D-ribofuranosylimidazole-4-*N*-benzyloxycarboxamide (**4**). Treatment of this with



methyl iodide in 0.1 *N* NaOH at room temperature did not give the expected methylmercapto derivative, but the odor of methylmercaptan was observed when the solution was acidified. The white, crystalline product obtained was assigned the structure **5** from its nmr and its subsequent hydrolysis products. In 32% HBr in glacial acetic acid **5** was hydrolyzed to 1-hydroxyguanine (**7**), and was hydrolyzed to 1-benzyloxyguanine (**6**) in refluxing 1 *N* HCl. Debenzylation of **6** with 32% HBr in glacial acetic acid gave 1-hydroxyguanine (Table I). Further proof of the structure of **7** was ob-

(1) This investigation was supported in part by funds from the National Cancer Institute (Grant No. CA 08748).

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(8) A. A. Watson, unpublished work.

(9) (a) J. A. Montgomery and H. J. Thomas, *J. Med. Chem.*, **15**, 1334 (1972) (personal communication prior to publication). (b) H. Sigel and H. Britziner, *Helv. Chim. Acta*, **48**, 433 (1965). (c) Pure 1-hydroxyinosine can be obtained by recrystallization from methanol to separate it from some salts, and chromatography over Dowex-50 (H^+) with water to eliminate a fluorescent impurity. F. L. Lam, private communication.

TABLE I
SPECTRAL DATA AND pK VALUES FOR 1-HYDROXYGUANINE[a]

pK_a	λ_{max}, nm	$\epsilon \times 10^{-3}$	pH	Charge
	275	7.20 ± 0.02		
	248	9.8 ± 0.1	1	+1
	208 (sh)	16.1 ± 0.2		
3.49 ± 0.11[b]				
	273	7.29 ± 0.01	5.23	0
	247	9.47 ± 0.02		
6.73 ± 0.07[b]				
	278 (sh)	5.96 ± 0.10		
	257	7.51 ± 0.10	9	−1
	227	30.4 ± 0.5		
11.51 ± 0.07[c]				
	278	7.4 ± 0.1		
	267 (sh)	7.2 ± 0.1	14	−2
	~225	~31.5 ± 0.1		

[a] Comparable pK values for 3-hydroxyguanine are 3.45, 5.97, and 10.67. From the 227-nm absorption band of the monoanion, it is apparent that the first ionization involves the *N*-hydroxy group, and the second the imidazole. Unlike 3-hydroxyguanine there is only one tautomeric form of the neutral species: J. C. Parham, T. G. Winn, and G. B. Brown, *J. Org. Chem.*, **36**, 2639 (1971). [b] By electrometric titration. [c] Spectrophotometrically, by methods described: A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962; D. D. Perrin, *Aust. J. Chem.*, **16**, 572 (1963).

tained by reduction to guanine in refluxing HI, and also by nitrosation to the known 1-hydroxyxanthine (**8**).

Experimental Section

The uv spectra were determined with a Unicam SP800 spectrophotometer, and the nmr spectra were determined in DMSO-d_6 (TMS) with a Varian A-60 spectrometer. Melting points were taken in a Mel-Temp apparatus. For thin layer chromatograms (tlc) Eastman chromatograph sheets with a silica gel layer containing a fluorescent indicator were used. The microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

1-Hydroxyinosine (**1**).—This was prepared according to the method of Montgomery,[9a] which avoids the requirement of DMF as a solvent.[4,9b] Adenosine 1-*N*-oxide (33.9 g) and $NaNO_2$ (82.8) were added to 1 l. of 29% aqueous acetic acid and the mixture was stirred for 1 or 2 days at room temperature. The acetic acid was removed by repeated extractions (300 ml each) with ether and the aqueous layer was evaporated at a bath temperature below 40°. The pH of the solution was adjusted from 3 to 4 with 1 *N* HCl and the resulting solution was evaporated to dryness. The residue was extracted with 300 ml of water. The product was collected, washed with water, and dried *in vacuo* over P_2O_5 to yield 11–17 g (33–54%) of off-white 1-hydroxyinosine, containing no adenosine 1-*N*-oxide, and of sufficient purity to be used in the next step.[9c]

Synthesis of 1-Benzyloxyinosine (**2**).—1-Hydroxyinosine (4.70 g, 0.013 mol) was stirred with benzyl bromide (3.81 g, 0.025 mol) and finely powdered K_2CO_3 (2.26 g) in 100 ml of dimethylformamide for 20 hr at 75°. The reaction mixture was cooled to room temperature and filtered, and the filtrate was evaporated to a yellow oil. The oil was triturated with 250 ml of hot acetonitrile and filtered to remove unreacted starting material. The filtrate was evaporated and the resulting residue was recrystallized from ethyl acetate and methanol to yield 3.06 g (50%) of colorless crystals, mp 189–191°, of 1-benzyloxyinosine: uv $\lambda_{max}^{pH\ 1}$ sh 244 nm (ϵ 9.74 × 10^3), 251 (10.9 × 10^3), sh 267 (6.08 × 10^3); $\lambda_{max}^{pH\ 13}$ sh 244 nm (ϵ 9.83 × 10^3), 251 (10.7 × 10^3), sh 267 (6.0 × 10^3); nmr δ 8.53 (s, 1, 2-CH), 8.47 (s, 1, 8-CH), 7.52 (m, 5, C_6H_5), 5.95 (d, 1, H-1′), 5.33 (s, 2, $C_6H_5CH_2$), 5.30 (b, 3, OH), 4.3 (m, 3, H-2′, H-3′, H-4′), 3–17 (broad s, 2, CH_2-5′).

Anal. Calcd for $C_{17}H_{18}N_4O_6 \cdot H_2O$: C, 52.19; H, 5.13; N, 14.27. Found: C, 52.19; H, 4.68; N, 14.22.

5-Amino-1-β-D-ribofuranosylimidazole-4-*N*-benzyloxycarboxamide (**3**).—The hydrolysis of 1-benzyloxyinosine was accomplished by refluxing **2** (3.06 g, 0.0082 mol) in 300 ml of ethanol and 75 ml of 6 *N* NaOH for 1.5 hr. The reaction mixture was evaporated at a bath temperature below 40° to 100 ml and carefully acidified to not less than pH 3 with 2 *N* HCl. The solution was cooled and filtered. The crystalline precipitate was washed with 50 ml of hot water and dried to yield 2.1 g (70%) of colorless cubes, mp 180–182°, of **3**: uv $\lambda_{max}^{pH\ 1}$ 275, sh 250 nm; $\lambda_{max}^{pH\ 13}$ 252 nm; nmr δ 10.70 (s, 1, CONH), 7.39 (m, 5, $C_6H_5CH_2$, 1,2-CH), 6.03 (broad s, 2, NH_2), 5.53 (d, H-1′), 5.30 (broad m, 3, OH), 4.90 (s, 2, CH_2), 4.12 (m, 3, H-2′, H-3′, H-4′), 3.63 (broad s, 2, CH_2-5′).

Anal. Calcd for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53; N, 15.37. Found: C, 52.76; H, 5.57; N, 15.22.

5-(*N*′-Benzoylthiocarbamoyl)amino-1-β-D-ribofuranosylimidazole-4-*N*-benzyloxycarboxamide (**4**).—5-Amino-1-β-D-ribofuranosyl-4-*N*-benzyloxycarboxamide (3.64 g, 0.01 mol) was dissolved in 100 ml of boiling acetone; then 100 ml of acetone solution containing 1.1 equiv of benzoyl isothiocyanate[10] was added.[7,11] The mixture was refluxed for ~3 hr, or until tlc run in 4:1 $CHCl_3$–MeOH and development in iodine showed no appreciable change in the reaction mixture.

The reaction mixture was evaporated *in vacuo* to an oil that was chromatographed over silica gel. Eluting with chloroform removed the unreacted benzoyl isothiocyanate and 9:1 $CHCl_3$–EtOH elution removed the starting material. $CHCl_3$–ethanol, 4:1, eluted the benzoylthioureido derivative **4**, which was obtained as a glass after the removal of the solvent: yield 2.16 g (41%); froths between 88 and 93°; uv λ_{max}^{EtOH} 239, sh 277 nm; nmr δ 8.1 (s, 1, 2-CH), 8.01 (m, 2, C_6H_5CO), 7.6 (m, 3, C_6H_5CO), 7.30 (s, 5, $C_6H_5CH_2$), 5.62 (d, 1, H-1′), 4.70 (m, 3, OH), 4.89 (s, 2, $C_6H_5CH_2$), 4.13 (m, 3, H-2′, H-3′, H-4′), 3.69 (broad s, 2, CH_2-5′), 11.21 (1, CONH), 11.99 (d, 2, NHCSNH–).

1-Benzyloxy-2-benzoylguanosine (**5**).—**4** (1.06 g, 0.002 mol) was stirred in 100 ml of 0.1 *N* NaOH until dissolved, then methyl iodide (0.5 ml) was added and stirring was continued for 18 hr. The solution was then acidified with acetic acid and the white precipitate was collected and washed with water. The white solid (**5**) recrystallized as white prisms from acetone–petroleum ether (bp 30–60°): yield 703 mg (71%); mp 174–175°; uv $\lambda_{max}^{pH\ 1}$ sh 235 nm (ϵ 14.0 × 10^3), 263 (11.2 × 10^3), 285 (11.3 × 10^3); $\lambda_{max}^{pH\ 13}$ 248 nm (ϵ 12.7 × 10^3), 263 (13.2 × 10^3), 268 (13.1 × 10^3); nmr δ 8.04 (s, 1, 8-CH), 7.9 (m, 2, C_6H_5CO), 7.6 (m, 3, C_6H_5CO), 7.31 (s, 5, $C_6H_5CH_2$), 5.85 (d, 1, H-1′), 5.30 (b, 3, OH), 5.20 (s, 2, $C_6H_5CH_2$), 4.2 (m, 3, H-2′, H-3′, H-4′), 3.60 (broad, 2, CH_2-5′), 11.00 (s, 1, CONH).

Anal. Calcd for $C_{24}H_{23}N_5O_7 \cdot H_2O$: C, 56.25; H, 5.07; N, 13.67. Found: C, 56.65; H, 4.80; N, 13.34.

1-Benzyloxyguanine (**6**).—**5** (205 mg, 4 × 10^{-4} mol) was refluxed in 20 ml of 1 *N* HCl for 1 hr. The solution was evaporated to dryness *in vacuo*. The residue was dissolved in 2 ml of methanol and chromatographed over Dowex-50. Benzoic acid was eluted with water, then a trace of 1-hydroxyguanine with 1 *N* HCl, and the main fraction with 2 *N* HCl. Recrystallization of the residue from the 2 *N* HCl fraction from methanol afforded white plates of 1-benzyloxyguanine hydrochloride: 95 mg (81%); uv $\lambda_{max}^{pH\ 1}$ 249 nm (ϵ 11.5 × 10^3), 278 (7.33 × 10^3); $\lambda_{max}^{pH\ 13}$ 257 nm (ϵ 7.81 × 10^3), 278 (8.4 × 10^3); nmr δ 9.0 (s, 1, 8-CH), 7.50 (m, 5, $C_6H_5CH_2$), 9.66 (m, 3, NH_3^+), 5.20 (s, 2, $C_6H_5CH_2$).

Anal. Calcd for $C_{12}H_{11}N_5O_2 \cdot HCl$: C, 49.07; H, 4.12; N, 23.84. Found: C, 49.19; H, 4.15; N, 23.73.

1-Hydroxyguanine (**7**). **A.**—1-Benzyloxy-2-benzoylguanosine (205 mg, 4 × 10^{-4} mol) was dissolved in 5 ml of warm glacial acetic acid, and 5 ml of 32% HBr in glacial acetic acid was added. The mixture was heated on a steam bath for 3.5 hr. The reaction mixture was then evaporated *in vacuo* and the residue was dissolved in a few milliliters of very dilute ammonia and chromatographed over Dowex-50. Elution with 1 *N* HCl gave the 1-hydroxyguanine, which was obtained as the hydrochloride on recrystallization from methanol and dried *in vacuo* over P_2O_5 at 78°, 63 mg (77%).

Anal. Calcd for $C_5H_5N_5O_2 \cdot HCl$: C, 29.50; H, 2.97; N, 34.40; Cl, 17.41. Found: C, 29.63; H, 3.14; N, 34.23; Cl, 17.39.

B.—The debenzylation of 6 (50 mg) was carried out as in A and the free base 7 was obtained from the hydrobromide salt by dissolving in hot dilute ammonia, treated with charcoal, and

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precipitated by the addition of glacial acetic acid. The white crystals were collected, washed with water, and dried *in vacuo* over P_2O_5 at 78°, 30 mg (74%).

1-Hydroxyxanthine.—To a cooled, stirred solution of 1-hydroxyguanine (10 mg) in 5 ml of 2 *N* HCl was added 1 ml of a 2 *M* solution of $NaNO_2$. After 8 hr the solution was evaporated to dryness and the residue was chromatographed over Dowex-50. The uv spectrum of the main fraction, eluted first with 1 *N* HCl, was identical with that of authentic 1-hydroxyxanthine.[5] Traces of 1-hydroxyguanine and an unidentified product were eluted with further 1 *N* HCl.

Guanine.—1-Hydroxyguanine (10 mg) was suspended in 1 ml of concentrated HI, warmed on a steam bath for 1 hr, and evaporated to dryness. The residue was chromatographed over Dowex-50. Elution with 1 *N* HCl removed a trace of unreduced 1-hydroxyguanine, and guanine, identified by its uv spectrum, was eluted with 2 *N* HCl.

Acknowledgment.—We thank Mr. Marvin J. Olsen for assistance with the nmr spectra, Mr. Gerald Reiser for the p*K* determinations, and Drs. James C. Parham and Gerhard Stöhrer for helpful discussions.

Registry No.—**1**, 5383-06-2; **2**, 40519-34-4; **3**, 40519-35-5; **4**, 40519-36-6; **5**, 40519-37-7; **6**, 40550-38-7; **7** hydrochloride, 40429-65-0; adenosine 1-*N*-oxide, 146-92-9; benzyl bromide, 100-39-0; benzoyl isothiocyanate, 4461-33-0.

Reaction of Thiete 1,1-Dioxide with α-Pyrone[1]

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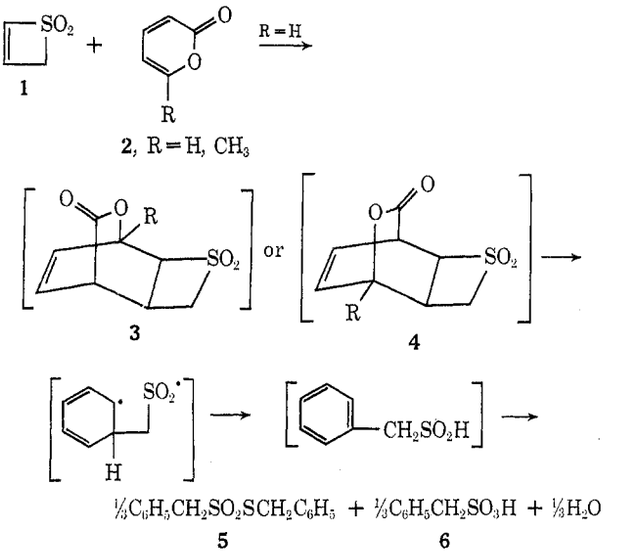
Received April 5, 1973

Thiete 1,1-dioxide (thiete sulfone)[2] behaves erratically in cycloaddition reactions. On the one hand it undergoes, in a normal fashion, additions of butadiene,[3] furans,[3,4] anthracene,[5] dienamines,[6] enamines,[6] ynamines,[6] and diazoalkanes.[7] On the other hand, the attempted Diels–Alder cycloaddition of tetraphenylcyclopentadienone to thiete sulfone resulted in evolution of sulfur dioxide and formation of a tetraphenylcycloheptatriene and a bicyclic octadienone in yields of 65 and 15%, respectively.[3]

α-Pyrone[8] is a reactive diene in Diels–Alder reactions and is a useful reagent for introducing the C_4H_4 moiety.[9] Treatment of thiete sulfone, **1** (10 mmol), with α-pyrone, **2** (10 mmol), under nitrogen in refluxing *m*-xylene for 24 hr gave benzyl α-toluenethiosulfonate, **5** (2.59 mmol), and benzylsulfonic acid, **6** (1.05 mmol),



instead of the expected product of the Diels–Alder cycloaddition. The properties of the α-toluene thiosulfonate were identical with those of an authentic sample prepared by oxidation of dibenzyl disulfide with hydrogen peroxide in acetic acid.[10] The benzylsulfonic acid was identified by conversion to benzylsulfonyl chloride, whose properties were identical with those of an authentic sample.[11] No reaction of thiete sulfone and α-pyrone was observed at 50° or 100°.

No reaction was observed between thiete sulfone and 6-methyl-2-pyrone[12] (**2**, R = CH_3) under the same conditions.

A possible scheme for the formation of benzyl α-toluenethiosulfonate involves the disproportionation of benzylsulfinic acid derived from the Diels–Alder adduct of α-pyrone and thiete sulfone. Although there are conflicting reports in the literature concerning the ease of disproportionation of benzylsulfinic acid, the conditions under which those disproportionation reactions were attempted were different from our conditions.[10,13,14] We have found that both benzyl α-toluenethiosulfonate (65.4%) and benzylsulfonic acid (40.8%) are formed when benzylsulfinic acid is refluxed in *m*-xylene for 30 hr. Disproportionation of sulfinic acids to thiosulfonates and sulfonic acids is well known and the mechanism has been established by Kice and his coworkers.[15] The possible involvement of free radicals in thermolysis of sulfones has been noted previously.[16]

The attempt to distinguish between possible inter-

(1) We are grateful to the National Institutes of Health for support of this work (Grant CA 08250).

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