to alkenes with bulky substituents, since the original rule 2 seems to hold for these cases.[12]

In addition to these two possible revisions, other proposals also need to be considered in future work. The aldehyde interchange mechanism[6] could be examined as an alternative way to rationalize the cis/trans cross ozonide ratio from propylene. It is plausible that the stereo effects involved in the attack of acetaldehyde on propylene molozonide and 2-butene molozonide could be different. Another aspect that could be considered is the stereo effects of intramolecular rearrangements within the solvent cage. Certainly the conformational results and propylene cross ozonide results presented here have raised a number of questions regarding the mechanism of ozonolysis that will need to be considered in future work.

(12) S. Fliszar and J. Renard, *Can. J. Chem.*, **48**, 3002 (1970).

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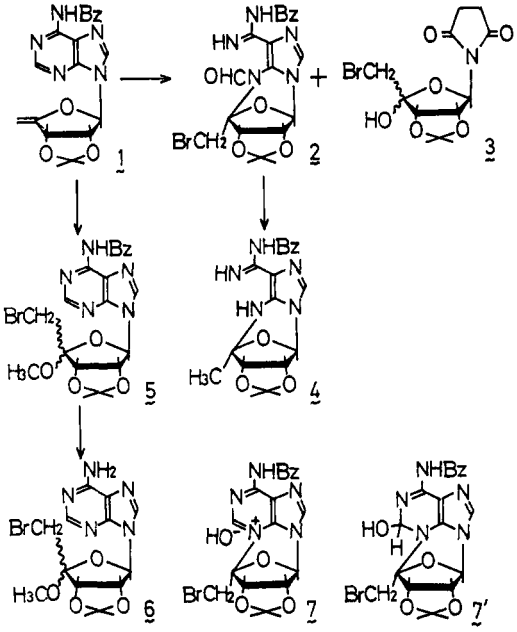
A Facile Cyclization–Decyclization Reaction of a 4′,5′-Didehydroadenosine Derivative. A New Route to the Chemical Modification of Adenosine

Sir:

In our project to exploit the synthetic utilities of didehydronucleosides, the introduction of a hydroxyl group into the 4′ position of nucleosides has drawn our interest to obtaining new types of biologically interesting compounds. Pertinent to the present purpose is the finding by Erickson, *et al.*,[1] that the addition reaction of hypobromous acid generated *in situ* from *N*-bromosuccinimide (NBS) and water is highly *regiospecific*. This report deals with the results obtained by applying the reagent to 6-benzamido-9-(5-deoxy-2,3-*O*-isopropylidene-β-D-*erythro*-pent-4-enofuranosyl)-purine (**1**).[2]

A mixture of equimolar **1** and NBS was stirred in an ice-cold mixture of water and dioxane for 1 hr. Extraction of the reaction mixture with ethyl acetate gave N^5,4′-anhydro-(5′-deoxy-5′-bromo-2′,3′-*O*-isopropylidene-α-L-lyxosyl)-4-benzoylcarboxamidino-5-(*N*-formyl)aminoimidazole (**2**)[3] (see Scheme I) as yellow needles in 20% yield: mp above 180° dec; λ_{max}^{EtOH} 334 (ε 18,100), 266 (ε 14,000), and 244 nm (ε 14,900); ir (KBr) 1685 ($\nu_{C=O}$) and 3360 cm^{-1} (ν_{NH}); nmr ($CDCl_3$) δ 1.34 (s, 3 H, methyl), 1.56 (s, 3 H, methyl), 3.75 (d, 1 H, J_{gem} = 10 Hz, $H_{5'a}$), 4.02 (d, 1 H, J_{gem} = 10 Hz, $H_{5'b}$), 4.84 (s, 2 H, $H_{2'}$ and $H_{3'}$), 5.94 (s, 1 H, $H_{1'}$), 7.10–8.35 (m, 8 H, Ph, NH, formyl, and C_2 H) and 10.20 (br s, 1 H, NH, lost on D_2O addition). The mother liquor of **2** was chromatographed on a silica gel column using chloroform–ethyl acetate (3:1) to give bromohydrin **3** in 12% yield from the first fraction: mp 147–149° (ether); no uv absorption at a wavelength above 220 nm; nmr ($CDCl_3$) δ 1.36 (s, 3 H, methyl), 1.57 (s, 3 H, methyl), 2.79 (s, 4 H, succinimide protons), 3.60 (s, 2 H, 5′-CH_2), 4.75 (d, 1 H, $J_{2',3'}$ = 6 Hz, $H_{3'}$), 5.18 (d of d, 1 H, $J_{2',3'}$ = 6 Hz, $J_{1',2'}$ = 1.8 Hz, $H_{2'}$), 5.42 (s, 1 H, OH, lost on D_2O addition), 5.78 (d, 1 H, $J_{1',2'}$ = 1.8 Hz, $H_{1'}$). The second and third fractions gave succinimide and N^6-benzoyladenine in yields of 21 and 35%, respectively. Atmospheric pressure reduction of **2** in the presence of Pd/C and succeeding preparative thin layer chromatography on the reaction mixture gave N^5,4′-anhydro-(5′-deoxy-2′,3′-*O*-isopropylidene-α-L-lyxosyl)-4-benzoylcarboxamidino-5-aminoimidazole (**4**) as pale yellow needles in 50% yield: mp 245–247°; ir (KBr) 1692 ($\nu_{C=O}$) and 3320 cm^{-1} (ν_{NH}); λ_{max}^{EtOH} 336 (ε 19,000), 266 (ε 13,900), and 244 nm (ε 15,000); nmr ($CDCl_3$) δ 1.32 (s, 3 H, methyl), 1.52 (s, 3 H, methyl), 1.77 (s, 3 H, 5′-methyl), 4.60 (d, 1 H, $J_{2',3'}$ = 5 Hz, $H_{2'}$ or $H_{3'}$), 4.77 (d, 1 H, $J_{2',3'}$ = 5 Hz, $H_{3'}$ or $H_{2'}$), 5.74 (s, 1 H, $H_{1'}$), 7.10–8.10 (m, 8 H, Ph, C_2 H, and two NH, two-proton part was lost on D_2O addition), and 9.90 (br s, 1 H, NH, D_2O exchangeable).

Scheme I

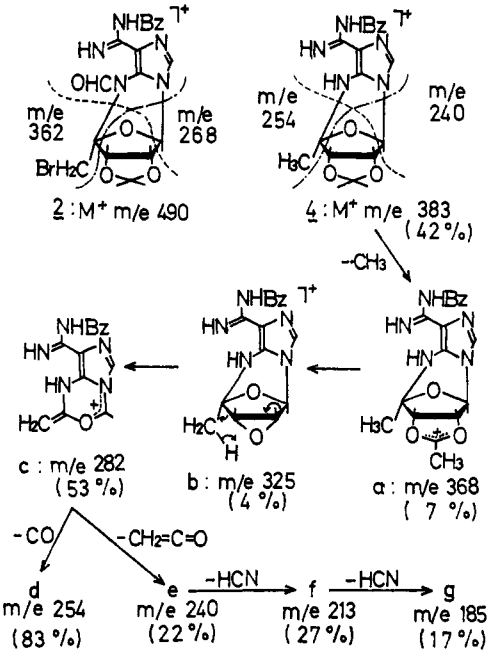


Final evidence for the acyclic nature of the base moiety and the N^5,4′ cyclic nature of compound **4** and hence of compound **2** was provided by mass spectrometry. In both cases, benzoyl cation (*m/e* 105) appeared as base peaks, which precluded a cyclic base-structure conjugated with a phenyl group for these compounds. Both compounds exhibited characteristic fragment ions produced by cleavages along the dotted and dashed lines as shown in Scheme II. Some plausible fragmentation patterns of **4** are also given therein (values in parentheses are relative intensities).

On the other hand, analogous reaction of **1** with NBS in methanol at room temperature overnight gave 9-(2′,3′-*O*-isopropylidene-4′-methoxy-4′-bromomethylene-β-D-erythrofuranosyl)-N^6-benzoyladenine (**5**) in 60% yield after silica gel column chromatography (chloroform) and recrystallization from benzene: mp 216–217°; ir (KBr) 1690 ($\nu_{C=O}$) and 3310 (ν_{NH}); λ_{max}^{EtOH} 277 (ε 17,400) and 230 nm (ε 11,800); nmr ($CDCl_3$) δ 1.45 (s, 3 H, methyl), 1.62 (s, 3 H, methyl), 2.92 (s, 3 H, 4′-methoxy), 3.50 (d, 1 H, J_{gem} = 10 Hz, $H_{5'a}$), 3.73 (d, 1 H, J_{gem} = 10 Hz, $H_{5'b}$), 4.91 (d, 1 H,

(1) K. L. Erickson and Kyongtae Kim, *J. Org. Chem.*, **36**, 2915 (1971).
(2) I. D. Jenkins, J. P. H. Verheyden, and J. G. Moffatt, *J. Amer. Chem. Soc.*, **93**, 4323 (1971).
(3) All new compounds gave satisfactory elemental analyses.

Scheme II



$J_{2',3'}$ = 6 Hz, $H_{3'}$), 5.47 (d, 1 H, $J_{2',3'}$ = 6 Hz, $H_{2'}$), 6.51 (s, 1 H, $H_{1'}$), 6.60–8.15 (m, 6 H, Ph and NH, one-proton part was D_2O exchangeable), 8.17 (s, 1 H, H_2), and 8.81 (s, 1 H, H_8). Treatment of **5** with methanolic ammonia at room temperature for 2 days and subsequent preparative thin layer chromatography gave 9-(2′,3′-*O*-isopropylidene-4′-methoxy-4′-bromomethylene-β-D-erythrofuranosyl)adenine (**6**) in 43% yield: mp 241–243°; ir (KBr) 3420 and 3320 cm^{-1} (ν_{NH}); λ_{max}^{EtOH} 258 nm (ε 13,300); nmr ($CDCl_3$) δ 1.41 (s, 3 H, methyl), 1.68 (s, 3 H, methyl), 3.48 (s, 3 H, 4′-methoxy), 3.70 (br s, 2 H, 5′-CH_2), 5.32 (s, 2 H, $H_{2'}$ and $H_{3'}$), 6.18 (s, 1 H, $H_{1'}$), 6.32 (br s, 2 H, NH_2, D_2O exchangeable), 7.95 (s, 1 H, H_2), and 8.38 (s, 1 H, H_8).[4]

Acid-catalyzed cleavage of adenine is known to give 4-aminoimidazole-5-carboxamidine[5] which can also be derived from adenine 3-*N*-oxide.[5] However, the hydrolysis conditions used are usually too vigorous to be applied to adenosine without depurination.[6] While in our case the plausible intermediate **7** or **7′** could not be isolated, their intermediacy seems to be probable on the basis of an observation that an ice-cold ethyl acetate extract of the reaction mixture became rapidly yellow colored on standing at room temperature.[7] The formation of **2** represents the first N,4′ cyclization with concomitant facile ring cleavage of the base moiety in purine nucleoside derivatives, and would provide a route to a new type of biologically interesting adenine nucleosides.[8]

(4) On heating compound **6** in *N*,*N*-dimethylformamide at 120° for 24 hr, there was no indication of quaternization at N_3, **6** being recovered unchanged.

(5) M. A. Stevens and G. B. Brown, *J. Amer. Chem. Soc.*, **80**, 2759 (1958).

(6) Interesting rearrangements of N^6-(α-aminoacyl)adenines to *N*-(6-purinyl)amino acids under neutral conditions are described [G. B. Chheda and R. H. Hall, *Biochemistry*, **5**, 2082 (1966)].

(7) Attempts to evaporate the solvent at below room temperature were unsuccessful due to a strong solvation which gave invariably heavy gelatinous precipitates.

(8) There was an indication that conjugative stabilization by the benzoyl group assisted the ring opening of the base, since the product of analogous reaction of hypobromous acid on 6-amino-9-(5-deoxy-2,3-*O*-isopropylidene-β-D-*erythro*-pent-4-enofuranosyl)purine showed a normal adenine absorption. Its complete separation and characterization have not yet been achieved.

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*Book Reviews**

Absorption Spectra in the UV and Visible Region. Volume XVI. Edited by L. LANG. Academic Press, New York, N. Y. 1972. 400 pp. $29.50.

Each page of this loose-leaf work shows a uv–visible spectrum graphically on one side, and overleaf in numerical form with log I_0/I at 2-mm intervals. The selection of spectra is a very mixed bag of mostly organic compounds, obtained from sixteen references from the period 1968–1972. The order appears to be random, but a separate booklet, carried Kangaroo fashion in a pocket in the back cover, has a name index and a formula index. The system for identifying the investigator responsible for each spectrum, which ought to be very simple for such a small number of sources, is unnecessarily complex and requires one to refer in succession to the figure number, then to the figure index, and then to the literature list. The figures themselves are commendably clear, and comparison is greatly aided by the fact that all are presented on the same scale.

Chemical Investigations for Changing Times. By L. W. SCOTT, L. M. ZABOROWSKI, J. W. HILL, and P. MUTO (University of Wisconsin, River Falls). Burgess Publishing Co., Minneapolis, Minn. 1972. ix + 173 pp. $4.25.

This is an unconventional laboratory manual suitable for an introductory course for students without previous instruction in chemistry. Its main thrust is to motivate students and to convey to those without a professional interest in science some of the enthusiasm that dedicated chemists have. It does so with such experiments as "Cathode Ray Tubes—The Jolly Green Electrons," "Density—Why Oil Floats when the Tanker Sinks," and "Hydrogen Chloride—How to Lose Your Marble." Most of the experiments are said to be readily adaptable for use as lecture demonstrations.

Environmental Engineering and Sanitation. Second Edition. By J. A. SALVATO, JR. Wiley-Interscience, New York, N. Y. 1972. xviii + 919 pp. $24.95.

The author states his aim to be to present in one volume a comprehensive treatment of the subject primarily for teachers and students, but also for all others concerned in some way with environmental health. The emphasis is on practical applications. Although chemistry pervades many of the chapters, it is necessarily handled at an elementary level. There is a very large amount of information of practical reference value presented in tables, from which one can learn, for example, that 0.40 mg/l. of copper sulfate in water is likely to kill catfish, and the average horse produces 12 tons (*sic!*) of "waste" per year. (The annual waste production of the average chemist is not stated.)

Metabolism of the Hypoxic and Ischaemic Heart. Edited by P. MORET and Z. FEJFAR. S. Karger AG/Albert J Phiebig Inc., P.O. Box 352, White Plains, N. Y. 1972. xii + 493 pp. $27.45.

The proceedings of a symposium on the title subject held in

* Unsigned book reviews are by the Book Review Editor.