3   4

(b) N_2 fixation by agents of the ferredoxin structural type.

After the slow addition of a THF solution of 3[8] (0.4 mmol in 100 ml) to a solution containing 2 equiv of 4 and 8 equiv of sodium naphthalenide (NaNp), all at room temperature, the reaction mixture was allowed to stir for 20 hr. Visible and infrared spectroscopy indicated that the NaNp was completely consumed prior to the addition of 3.[9] After the addition of 20% aqueous HCl,[11] solvent was removed and the NH_4Cl was extracted from the residue with H_2O. Nessler tests were positive, and the NH_3 yields as determined by the Kjeldahl method[12] ranged from 0.013 to 0.044 mmol/mmol of 3.[13] Ammonia yields were also measured using an NH_3 gas electrode,[14] and fell at levels at least 85% of those determined by the Kjeldahl method. When a reduction of 3 was carried out as above, but in the presence of 16 equiv of NaNp, the yield rose to as high as 0.268 mmol of NH_3/mmol of 3.

Additional novel N_2 fixations were uncovered which bear on the reaction pathway involving 3 and 4. The Mo complex 3 itself, although produced in the presence of metallic Mg or Na·Hg,[4a,b] is reducible by excess NaNp to ammonia (0.100–0.300 mmol of NH_3/mmol of 3) as are $[Mo(N_2)_2(dppe)_2]^+I_3^-$ [15] (0.040–0.085) $ReClN_2(dppe)_2$[16] (0.017–0.025), and $IrClN_2(PPh_3)_2$[17]

Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, J. Amer. Chem. Soc., 91, 1551 (1969); (b) J. E. Bercaw and H. H. Brintzinger, ibid., 93, 2045 (1971); (c) R. H. Marvich and H. H. Brintzinger, ibid., 93, 2046 (1971); (d) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, ibid., 94, 1218 (1972); (e) E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, J. Chem. Soc., Chem. Commun., 481 (1972).

(7) (a) For the HCl-promoted conversion of 3 to $MoCl_2(N_2H_2(dppe)_2$, see J. Chatt, G. A. Heath, and R. L. Richards, ibid., 1010 (1972); (b) in the case of NH_3 formation by reaction of $(PPh_3)_3CoH(N_2)$, naphthalene, Li, and $TiCl_4$ (or $MoCl_5$, $CoCl_2$, $FeCl_3$), reported by M. E. Vol'pin, V. S. Lenenko, and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim., 2, 463 (1971), transfer of the N_2 ligand from Co to Ti, followed by reduction of Ti-bound N_2,[6] was not ruled out.

(8) Water and oxygen were removed from THF by distillation under argon from sodium benzophenone ketyl. All experiments were conducted under argon, unless noted, using standard vacuum line techniques.

(9) From polarographic data[5,10] it can be inferred that 4 will react with 4 equiv of NaNp to produce 4^{4-}.

(10) S. Wawzonek and H. A. Laitinen, J. Amer. Chem. Soc., 64, 2365 (1942).

(11) Purified by distillation. All other aqueous reagents utilized in the work-up were prepared from doubly distilled degassed water.

(12) Titrations were followed potentiometrically and yields were graphically determined from ca. 20 data points. Each was corrected for a small blank.

(13) All experiments were conducted at least in triplicate and the full range of yields is reported.

(14) An Orion Model 95-10 ammonia gas electrode was utilized, and the yields were determined by known additions of standard NH_4Cl solutions, the original concentrations being extrapolated using 100% volume corrected Gran's Plot Paper.

(15) T. A. George and C. D. Seibold, J. Amer. Chem. Soc., 94, 6859 (1972); dppe = 1,2-bisdiphenylphosphinoethane.

(16) J. Chatt, J. R. Dilworth, and G. J. Leigh, Chem. Commun., 687 (1969).

(17) J. P. Collman and J. W. Kang, J. Amer. Chem. Soc., 88, 3459 (1966).

(0.065–0.100), substances of the type previously considered refractory toward reducing agents with a potential up to and including that of metallic Na.[18] No N_2H_4 formation was observed in any of these reductions, and NaNp per se does not of course fix N_2. Further, the iron–dithiolene system 4 alone is capable of fixing molecular N_2. At the 4— level, this inorganic agent, under a N_2 atmosphere or in the presence of 2 equiv of N_2 rapidly circulated through the solution under argon, led to formation of up to 0.137 mmol of NH_3/mmol of 4^{4-}. When a ca. 300 molar excess of NaNp was added to 4 under N_2, yields rose to 0.259–0.269 mmol of NH_3/mmol of 4. Similar fixation results were secured with the Fe–S cluster $(FeSC_5H_5)_4$.[19]

In consideration of the yield data herein, preliminary rate data on N_2 dissociation from $Mo(N_2)_2(dppe)_2$ in THF, and the evidence that 3 undergoes ready conversion with CO to $Mo(CO)_2(dppe)_2$ by means of first-order loss of N_2 followed by CO combination,[4c] we believe it likely that NH_3 formation from 3 and 4^{n-} involves predominant initial release of N_2 from 3, followed by coordination and reduction by 4^{n-}. At the present time little evidence as to the detailed chemical mechanism of biological N_2 coordination–reduction is available, and overall enzymic fixation by initial N_2 coordination followed by transfer of N_2 to the reduction site remains a distinct possibility.

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Mechanism of Ozonolysis. Conformations of Propylene and trans-2-Butene Ozonides[1]

Sir:

In a previous report[2] it was shown that ethylene ozonide has the O–O half-chair conformation with C_2 symmetry. We have now determined that propylene and trans-2-butene ozonides have the same half-chair conformation as ethylene ozonide. This observed conformation is different from that postulated by the Bauld–Bailey syn–anti zwitterion mechanism for final ozonides with bulky substituents.[3] We have also found that the cis/trans ratio for 2-butene ozonide obtained as a cross ozonide from propylene differs significantly from that obtained as a normal ozonide from cis- or trans-2-butene. The syn–anti zwitterion mechanism is

reviewed in the light of these data and two possible revisions are considered.

Propylene and *trans*-2-butene ozonides were prepared using techniques described previously.[2] Ozonolyses were carried out to ~70% completion in isobutane solvent at −95°, with fast warm-up.[4] Using gas chromatography, cross ozonides (~15%) were separated from propylene ozonide, and the trans isomer of 2-butene ozonide was separated from the cis isomer (the trans isomer had the shorter retention time). While the cis/trans ratio of 2-butene ozonide obtained as the normal ozonide was less than unity as reported previously,[5] this ratio obtained as a cross ozonide from propylene was rather surprisingly greater than unity (~80/20).

The ozonide conformations were determined using microwave spectroscopy. The following rotational constants (in MHz) were obtained: $A = 7574.36 \pm 0.02$, $B = 3476.33 \pm 0.01$, and $C = 2644.79 \pm 0.01$ for propylene ozonide and $A = 6022.05 \pm 0.03$, $B = 2103.08 \pm 0.02$, and $C = 1695.66 \pm 0.02$ for *trans*-2-butene ozonide. Neither species showed any effect from pseudorotation or methyl internal rotation.

The conformations of the ozonides were established by comparing the observed rotational constants with those calculated from structural parameters extrapolated from ethylene ozonide. These calculations showed unambiguously that the observed constants are consistent only with the equatorial isomer for propylene ozonide and the biequatorial isomer for *trans*-2-butene ozonide with a half-chair conformation for the ring analogous to ethylene ozonide. The observed dipole components and the rotational constants for several isotopically enriched species also agree with this. Thus far no transitions arising from the axial isomer of propylene ozonide or the biaxial isomer of *trans*-2-butene ozonide have been assigned. These isomers are apparently less abundant, although it is difficult at this time to place an upper limit on their concentrations.

These results are quite interesting with regard to the mechanism of ozonolysis. The Bauld–Bailey syn–anti zwitterion mechanism will be principally discussed here.[3] Of recently proposed mechanisms,[3,6,7] it alone explicitly discusses the conformation of the final ozonide. The stereochemical course of ozonide formation as predicted by this mechanism is governed by three rules which are summarized in Table I of ref 3. Rule 3 of that proposal postulates that the final ozonide has a C–O half-chair conformation. Although this conformation may be correct for final ozonides with bulky substituents, our results show that the ozonides of ethylene, propylene, and *trans*-2-butene have the O–O half-chair conformation. With this conformation, diaxial or diequatorial substituents are trans and axial-equatorial substituents are cis, contrary to rule 3 in the original proposal. The obvious implication is that rule

3, at least for methyl groups, must be revised in order to agree with the observed conformations.

It is interesting to consider possible revisions of the syn–anti mechanism that will be compatible with the new experimental data for methyl substituents. We find two alternatives. One revision is to retain the basic postulates of the three rules but to amend the third rule so that ozonides with a,a or e,e substituents have the trans configuration while those with a,e substituents have the cis configuration. The revised mechanism for the ozonolysis of 2-butene would be as follows. *cis*-2-Butene forms a *cis*-1,2,3-trioxolane primary ozonide (C–C half-chair) with the a,e conformation. *trans*-2-Butene forms a trans primary ozonide; however, the e,e conformation is preferred for small substituents.[3,8] Following rules 1 and 2 the predominant zwitterion configuration will be anti for both the cis (a,e) and trans (e,e) primary ozonides. Finally applying the revised rule 3, anti zwitterions react preferentially with acetaldehyde to give predominantly the trans (e,e) conformation in the final ozonide. Consequently, both *cis*- and *trans*-2-butene should yield more trans than cis final ozonide, which is in agreement with the observed cis/trans ratios.[5]

This revision retains most of the original mechanism and is consistent with known final ozonide conformations. The revision also rationalizes the low cis/trans ratios obtained from alkenes with small substituents (methyl, ethyl, or *n*-propyl);[5] these data were difficult to account for within the original proposal.[3] The revision is deficient, however, in rationalizing the high cis/trans ratio in the cross ozonide of propylene; it also cannot be readily extrapolated to explain the cis/trans ratios when bulky groups are attached.

Another interesting revision is possible involving changes in both rules 2 and 3. Rule 2 states that equatorial substituents are incorporated into the zwitterion moiety in preference to axial substituents.[3] Fliszár, *et al.*,[9,10] have suggested that *cis*-2-butene primary ozonide may be an exception to this rule; *i.e.*, the axial methyl group in this molozonide may be preferentially incorporated into zwitterions, giving a predominance of syn rather than anti zwitterions (*via* rule 1). With regard to *trans*-2-butene primary ozonide, MO calculations suggest that the a,a and e,e forms are similar in energy;[8] possibly they exist together in equilibrium. If one further postulates that the a,a isomer cleaves at a faster rate, a predominance of syn zwitterions will be formed. Syn zwitterions react with acetaldehyde to give mainly trans final ozonide (rule 3), except that the final conformation is e,e rather than a,e as in the original proposal.[3]

This second revision can be extended to other small olefins using arguments similar to those given above for 2-butene. This alternative also has the advantage of being able to rationalize the high cis/trans ratio in the cross ozonide of propylene, assuming the methyl group is equatorial in the primary ozonide.[11] Furthermore, the original Bauld–Bailey mechanism[3] (with perhaps a revised final ozonide conformation) can still be applied

(4) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1098 (1971).

(5) F. L. Greenwood, *J. Amer. Chem. Soc.*, **88**, 3146 (1966); R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(6) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **88**, 3143 (1966); P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966); P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968)

(7) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *ibid.*, **93**, 3044 (1971); P. R. Story, E. A. Whited, and J. A. Alford, *ibid.*, **94**, 2143 (1972).

(8) J. Renard and S. Fliszár, *ibid.*, **92**, 2628 (1970).

(9) S. Fliszár, J. Renard, and D. Z. Simon, *ibid.*, **93**, 6953 (1971).

(10) S. Fliszár, *ibid.*, **94**, 7386 (1972).

(11) EHT calculations (ref 8) favor an equatorial methyl group in propylene primary ozonide.

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*-isopropyl-idene-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 (CDCl₃) δ 1.34 (s, 3 H, methyl), 1.56 (s, 3 H, methyl), 3.75 (d, 1 H, J_{gem} = 10 Hz, H₅′ₐ), 4.02 (d, 1 H, J_{gem} = 10 Hz, H₅′ᵦ), 4.84 (s, 2 H, H₂′ and H₃′), 5.94 (s, 1 H, H₁′), 7.10–8.35 (m, 8 H, Ph, NH, formyl, and C₂ H) and 10.20 (br s, 1 H, NH, lost on D₂O 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 (CDCl₃) δ 1.36 (s, 3 H, methyl), 1.57 (s, 3 H, methyl), 2.79 (s, 4 H, succinimide

(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 I
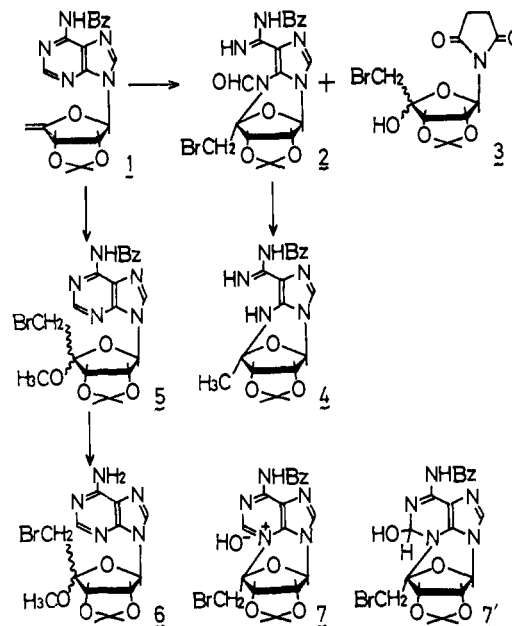
protons), 3.60 (s, 2 H, 5′-CH₂), 4.75 (d, 1 H, $J_{2′,3′}$ = 6 Hz, H₃′), 5.18 (d of d, 1 H, $J_{2′,3′}$ = 6 Hz, $J_{1′,2′}$ = 1.8 Hz, H₂′), 5.42 (s, 1 H, OH, lost on D₂O addition), 5.78 (d, 1 H, $J_{1′,2′}$ = 1.8 Hz, H₁′). The second and third fractions gave succinimide and N^6-benzoyladenine in yields 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-benzoylcarbox-amidino-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 (CDCl₃) 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, H₂′ or H₃′), 4.77 (d, 1 H, $J_{2′,3′}$ = 5 Hz, H₃′ or H₂′), 5.74 (s, 1 H, H₁′), 7.10–8.10 (m, 8 H, Ph, C₂ H, and two NH, two-proton part was lost on D₂O addition), and 9.90 (br s, 1 H, NH, D₂O exchangeable).

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′-bromomethyl-ene-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 (CDCl₃) 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, H₅′ₐ), 3.73 (d, 1 H, J_{gem} = 10 Hz, H₅′ᵦ), 4.91 (d, 1 H,