

TABLE I

Compound ^a	M.p., ° C. ^b	[α] _D ²⁵ (g./100 ml. H ₂ O)	R _f ^c	Ultraviolet spectra ^d			
				0.1 HCl		0.1 NaOH	
				λ _{max.} mμ	ε × 10 ⁻¹	λ _{max.} mμ	ε × 10 ⁻¹
1	246	-84.9 ± 0.2 (0.351)	0.19	272	13.6	270	9.8
11	220-222	0 (0.397)	.15	273	13.3	271	9.9
Nucleoside from ψ- B ₁₂ ^e	218-222	0 ^f (0.262)	.15 ^g	273	13.6	271	9.8
Adenosine ^h	233	-60.4 (0.7)	.20	260	14.2	260	14.3
9-α-D-Ribofuranosyl- adenine ^h	201	+24 (0.65)	.17	257			
111	275-277		.75	275	17.5	272	12.2
1V	216		.89	300	28.2	231 ^h	17.0
V ⁱ	278					333	17.9
V11			.31	278	14.3	281	11.5

^a Satisfactory elemental analyses (C, H, N) were obtained for each compound except V11, which was not analyzed. ^b Melting points below 260° were determined on a Kofler Heizbank; those above 260° were determined in a capillary and are uncorrected. ^c Whatman No. 1 paper, water-saturated butanol. ^d Determined with a Cary Model 14 spectrophotometer. ^e Data from ref. 3. ^f Temperature not specified. ^g Calcd. from R_{adenosine}. ^h Data from ref. 14. ⁱ Elemental analyses show that V is a dipurinylmercury.

of crude 3-benzyl-7-β-D-ribofuranosyladenine (VII) was obtained as a brown glass. The benzyl group of this nucleoside VII was removed by hydrogenolysis using 5% palladium-on-charcoal catalyst in a mixture of ethanol and water at 80° and 47 p.s.i. of hydrogen. The resulting nucleoside, obtained in 31% yield, was identified as 7-β-D-ribofuranosyladenine (I) by its ultraviolet spectrum (showing sugar attachment at N-7) and application of the *trans* rule⁹ (indicating the configuration of the glycosyl linkage formed by this coupling must be β¹⁰).

Coupling of the same dipurinyl mercury V with 5-O-benzoyl-D-ribofuranosyl bromide 2,3-cyclic carbonate¹³ followed by deblocking of the resultant nucleosides with methanolic sodium methoxide gave a mixture of 3-benzyl-7-β-D-ribofuranosyladenine (VII) and 3-benzyl-7-α-D-ribofuranosyladenine (VIII) which could not be separated but could be debenzylated catalytically as described earlier for the β-anomer. Partition chromatography of the resulting mixture, using a cellulose powder column and butanol-water (86:14), gave first 7-β-D-ribofuranosyladenine (I), which crystallized on seeding with a crystal of material obtained from the first coupling described earlier, and then 7-α-D-ribofuranosyladenine (II), purified through its picrate.

Properties of the anomeric nucleosides and some of their precursors are given in Table I, along with those of the nucleoside from pseudovitamin B₁₂, adenosine, and its α-anomer. The samples of the β-anomer I prepared by the two different coupling reactions were identical, whereas the properties of the α-anomer II are in good agreement with those reported for the nucleoside from pseudovitamin B₁₂.³ The optical rotations of the anomers (β, -84.9 ± 0.2°; α, 0°) confirm the assignment of α- and β-configurations and agree well with the relative values for adenosine and its α-anomer (-60.4° and +24°).

(9) B. R. Baker, *Ciba Found. Symp., Chem. Biol. Purines*, 120 (1957).

(10) No true exceptions to the *trans* rule have been reported in the synthesis of purine nucleosides.¹¹ In rare instances a minor amount of α-anomer has been detected¹² but the β-anomer is always the principal product of the reaction. In our reaction only one anomer could be detected.

(11) J. A. Montgomery and H. J. Thomas, *Advan. Carbohydrate Chem.*, **17**, 301 (1962).

(12) B. R. Baker, R. E. Schaub, and H. M. Kissman, *J. Am. Chem. Soc.*, **77**, 5911 (1955); H. M. Kissman and B. R. Baker, *ibid.*, **79**, 5534 (1957).

(13) This ribose derivative, which contains no acyloxy group at C-2 to cause stereospecific entry of a purine at C-1⁹ giving rise to a β-ribonucleoside only, has been used to prepare a mixture of adenosine and its α-anomer.¹⁴

(14) R. S. Wright, G. M. Tener, and H. G. Khorana, *J. Am. Chem. Soc.*, **80**, 2004 (1958).

It is now possible to state with certainty that the nucleoside moiety of pseudovitamin B₁₂ is in fact 7-α-D-ribofuranosyladenine. Synthesis of the nucleosides from other B₁₂ vitamins is in progress.

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A Two-Stage, Two-Center Decarboxylation¹

Sir:

The elusive question of simultaneity in multicenter-type reactions continues to receive its most critical examination in studies of Diels-Alder reactions.² Suggestions that a range of transition state structures might be accessible^{2b,c} are supported by results which clearly demonstrate the polar ambivalence of such states³ and warn that classical elucidative techniques might well distort the very phenomena they seek to measure.⁴ The dilemma can be avoided by isotopic substitution, preferably at the reaction sites but also^{2d,5} at adjacent atoms. Interpretations of these latter, α-hydrogen isotope effects have been rendered ambiguous by the discovery^{6a} of one clear exception to what had been regarded^{6b} as a universal, though necessarily empirical pattern. Less equivocal decisions should follow from determination of *primary* isotope effects at *both* reaction sites and we here report the first such investigation in this area.⁷

Thermal decarboxylation of the α-pyrone-maleic anhydride adduct⁸ was chosen for study assuming (a) that this might legitimately be regarded as a Diels-Alder retrogression and (b) that the structural sim-

(1) The study was supported by the Air Force Office of Scientific Research, under Contract No. 49(038)-942 and Grant No. 142-63.

(2) (a) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); (b) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961); (c) C. Walling and H. J. Schugar, *ibid.*, **85**, 607 (1963); (d) S. Seltzer, *ibid.*, **85**, 1360 (1963).

(3) J. Sauer and H. Wiest, *Angew. Chem.*, **74**, 353 (1962).

(4) This has been clearly recognized in the study of rate dependence on pressure (C. Walling and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 612 (1963)).

(5) (a) D. E. Van Sickle, *Tetrahedron Letters*, **687** (1961); (b) S. Seltzer, *ibid.*, 457 (1962).

(6) (a) R. E. Weston, Jr., and S. Seltzer, *J. Phys. Chem.*, **66**, 2192 (1962); (b) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2025 (1961); *ibid.*, **85**, 14 (1963).

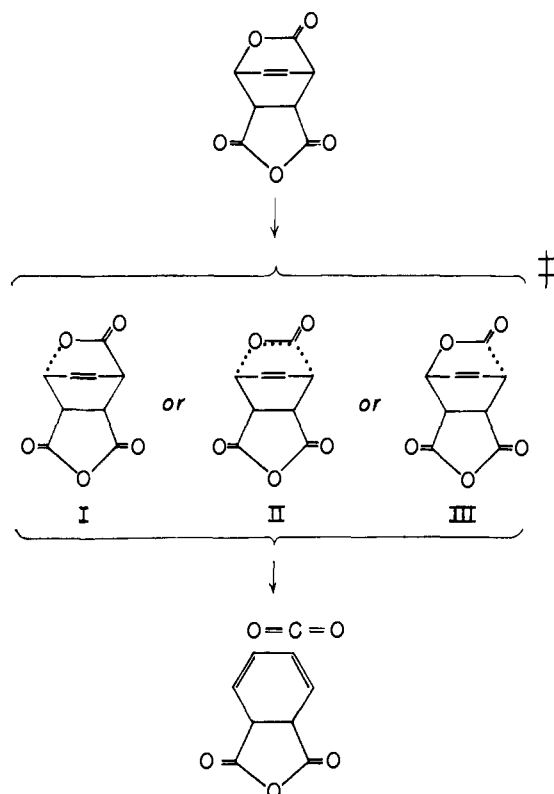
(7) (a) G. A. Ropp, V. F. Raen, and A. J. Weinberger, *ibid.*, **75**, 3697 (1953); (b) R. F. W. Bader and A. N. Bourns, *Can. J. Chem.*, **39**, 3448 (1961), are the most closely related studies in object (a) and approach (b).

(8) (a) O. Diels and K. Alder, *Ann. Chem.*, **490**, 257 (1931); (b) B. R. Landau, Ph.D. Thesis, Harvard University, 1950.

plicity of the dienophilic fragment might simplify interpretation of the experimental results. Kinetic analysis, C^{14} tracer studies, product isolation, and structure proof are in accord with the first assumption but will be described more fully at another time. C^{13} and O^{18} isotope effects were both determined at levels of natural abundance by consecutive mass spectral analyses of purified CO_2 obtained (a) after 5–10% reaction, (b) after ten half-lives, and (c) from a commercial cylinder.⁹ The results in Table I, column 2, have been corrected for instrumental "mass discrimination" and O^{17} contribution to the $m/e = 45$ peak. Other corrections were evaluated but then ignored when they proved to be less than the experimental uncertainty. These include: instrumental background, incomplete mass resolution, isotopic fractionation and/or exchange during CO_2 purification, O^{17} fractionation during decarboxylation, and C^{13} content in the $C_8H_6O_3$ fragment.

TABLE I

	Observed	Predicted	
		IIIA	IIIB
k_{12}/k_{13}	1.032 ± 0.001	1.0298	1.0293
k_{18}/k_{16}	1.015 ± 0.002	1.0155	1.0222
$\nu^\ddagger/\nu^\ddagger_C$		1.0073	1.0068
$\nu^\ddagger/\nu^\ddagger_O$		1.0023	1.0000
$\nu^\ddagger/\nu^\ddagger_{O'}$		1.0290	1.0455



These results are most simply analyzed in terms of the idealized transition states I, II, and III. Thus, the observed k_{12}/k_{13} is sufficiently similar to those obtained in reactions where C–C cleavage is unambiguous¹⁰ as to exclude I from further consideration.

II, however, requires more quantitative evaluation and, since we would have it encompass a wider range of possible structures, a more careful definition. This

(9) A Consolidated Engineering Corporation 21-401 mass spectrometer was used in its isotope ratio recording mode. Individual sample analyses were reproducible to ± 0.02 – 0.05% for C and ± 0.03 – 0.08% for O. Calculated isotope effects derive from five independent experiments for those of carbon and from three for those of oxygen. The solvent was dimethyl phthalate and the temperature was 130.1° .

(10) Malonic acid, 138° , 1.037; mesitoic acid 92° , 1.032; trichloroacetate ion, 70° , 1.034.^{11a} By contrast: xanthate pyrolysis, 100° , 1.000.^{7b}

is conveniently taken to be a common decomposition mode, the separation of rigid OCO' and $C_8H_6O_3$ along an axis joining their centers of mass. Mass dependence of the corresponding frequency (ν^\ddagger) is thereby determined¹² and we may use the $\tilde{\gamma}$ -method^{11b} and both our observed isotope effects to estimate the relative degrees of bond stretching at the two sites.¹³

$$\sum \frac{1/2(\Delta a^\ddagger_O + \Delta a^\ddagger_{O'})}{\Delta a^\ddagger_C} = \frac{\left(\frac{1}{12} - \frac{1}{13}\right) \left(\frac{k_{16}/k_{18}}{\nu^\ddagger/\nu^\ddagger_{O'}} - 1\right)}{\left(\frac{1}{16} - \frac{1}{18}\right) \left(\frac{k_{12}/k_{13}}{\nu^\ddagger/\nu^\ddagger_C} - 1\right)}$$

Although it might have been anticipated that the ratio (of mean changes in force constants at oxygen to those at carbon) would be somewhat less than one,¹⁴ the calculated value is -0.10 ± 0.09 . Whether truly negative or zero, the result is sufficiently irreconcilable with the decomposition mode used to generate it as to preclude further realistic discussion of any such transition state.

Left only with III, defined by $\Delta a^\ddagger_O = \Delta a^\ddagger_{O'} = 0$, we need but choose an appropriate decomposition mode to predict k_{16}/k_{18} and so consider two possibilities: A, in which rigid OCO' and $C_8H_6O_3$ unfold about a stationary bridgehead pivot, during C–C cleavage, and B, in which O serves as pivot.¹⁵ Prediction of k_{12}/k_{13} is inherently less reliable in this case since it requires the further *ad hoc* assignment of Δa^\ddagger_C and net frequency change. The traditional^{12b} values of -4.50 mdynes/Å. and 900 cm^{-1} were chosen both to avoid prejudice and to permit comparison with the evaluation of similar assumptions elsewhere.¹⁶

Table I clearly reveals IIIA to be the simplest description of the transition state consistent with both isotope effects. Obvious extensions of this technique to related systems are being pursued.

(11) (a) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 68 (1958); (b) *ibid.*, **1**, 18–26, 67 (1958).

(12) M. Wolfsberg, *J. Chem. Phys.*, **33**, 21 (1960).

(13) Δa^\ddagger_C , Δa^\ddagger_O , and $\Delta a^\ddagger_{O'}$ are the activation changes in diagonal cartesian force constants, at the carbonyl carbon, alkyl oxygen, and carbonyl oxygen, along any one of the three axes, and the sum is taken over all three axes. Subscripts following ν^\ddagger refer to the molecule bearing the heavier isotope at the position indicated. Zero time reaction and isotopic homogeneity of O and O', are implicitly assumed and can be justified under our conditions.

(14) Thermochemical data require that the CH_3 –C bond in methyl acetate be weaker than the CH_3 –O by some 2–14 kcal./mole.

(15) These provide the ν^\ddagger ratios by analogy with mechanical models. Cf. J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953); *ibid.*, **22**, 1264 (1954); P. Yankwich and R. M. Ikeda, *J. Am. Chem. Soc.*, **81**, 1532 (1959).

(16) M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, in press.

(17) Union Carbide Corporation Research Fellow, 1962–1963.

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A New Boron Hydride Ion $B_9H_{14}^-$

Sir:

Decaborane is degraded in aqueous base to boric acid, hydrogen, and a new, stable boron hydride ion of the composition $B_9H_{14}^-$. The possibility that such an ion might exist has been discussed¹ and, in two instances, ultraviolet absorption maxima were observed² which we now suspect were due to its presence. Salts containing the anion have now been isolated and the anion has been characterized by analyses, by conversion to known compounds, and by determination of the stoichiometry of the preparative reaction.

(1) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961); W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **47**, 1791 (1961).

(2) G. W. Schaeffer, J. J. Burns, T. J. Kligen, L. A. Martincheck, and R. W. Rozett, Abstracts of Papers, 135th National Meeting of the American Chemical Society, April, 1959, p. 44M; M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 1825 (1960).