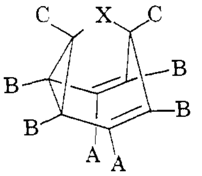
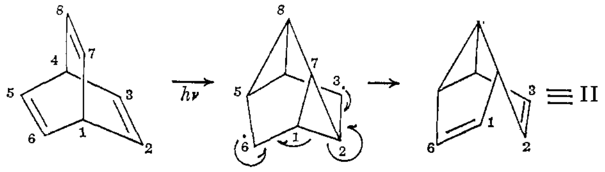
Table I. Nuclear Magnetic Resonance Data

Type H	Compd	τ^a	Ref	
A	II	4.92	Presently[b]	
	VII	4.3	2a	
	VIII	4.37	3[c]	
B	II	5.83	Presently[b]	II, X = zero carbon bridge
	VII	5.8	2a	VII, X = carbonyl bridge
	VIII	6.32	3[c]	VIII, X = $-CH_2CH_2-$ bridge
C	II	7.03	Presently[b]	
	VII	7.3	10[d]	
	VIII	8.1	3[c]	

[a] Multiplets in each case. [b] CCl_4. [c] CS_2. [d] Acetone-d_6.

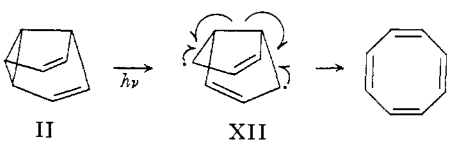
hydrobullvalene (VIII),[3] semibullvalene exhibited no nmr change to −110°. This contrasts with VII and VIII, where valence tautomerism is inhibited. The exciting possibility that IIa and IIb might instead be resonance contributors to a symmetrical species X seems ruled out by the ultraviolet spectrum (shoulder at 225–235 mμ (ε 2450)), which is quite similar to that reported[3] for dihydrobullvalene, and by the normal nmr.

The photochemical formation of semibullvalene from barrelene seems to involve three molecular processes: (i) 2,7 plus 5,8 bonding in barrelene; (ii) 1,2 bond fission; and (iii) triplet–singlet spin inversion. The extent to which the first two are concerted and the stage at which spin inversion occurs will be discussed later;[11] however, for simple presentation these are depicted as separate.



I XI (4)

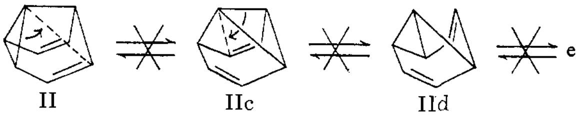
Photolysis of semibullvalene (II) itself was found to afford cyclooctatetraene but no barrelene. This may be pictured as[12]



II XII (5)

where XII may have no real existence.

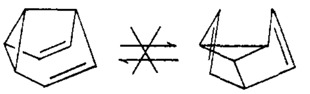
There are two further types of valence tautomerism which II might be envisioned as undergoing but does not. First is the vinylcyclopropane valence tautomerism considered by Viehe.[13] This would lead to a single nmr line as a result of the tautomerism of eq 6 and that of eq 3. However, the valence tautomerism of



II IIc IId (6)

eq 6 involves a four-center, four-electron "cyclobutadienoid" transition state (all front lobes overlapping) and should be energetically unfavorable.

The last type of valence tautomerism in eq 7 is considered, since as far as the atomic nuclei are concerned the top and bottom of semibullvalene are nearly equivalent. Such tautomerism would lead in the extreme to two nmr peaks. The close approximation of the



II IIe (7)

three nmr bands of II to models (Table I) coupled with the low-temperature nmr rules out this exciting potentiality.

Future publications will deal with the chemistry of semibullvalene and the mechanistic aspects of the interconversions described presently.

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Howard E. Zimmerman, Gary L. Grunewald
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706
Received November 18, 1965

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(11) It seems likely that spin interconversion and 1,2-bond fission precede completion of the 2,7 and 5,8 bonding, so that the biradical species XI does not fully develop.

(12) Alternative mechanisms may be written and will be discussed subsequently. As in the barrelene reaction, there is an intriguing reaction coordinate–MO correlation.

(13) H. G. Viehe, *Angew. Chem.*, 77, 768 (1965); the structure II was cited as of interest and the name "octavalene" suggested.

Manganese–Hydrogen Bond Distance in $HMn(CO)_5$

Sir:

We wish to report the measurement of the manganese hydrogen bond distance (1.28 ± 0.01 A) in manganese pentacarbonyl hydride, $HMn(CO)_5$. This measurement is of particular significance in view of the recent interest and speculation concerning transition metal hydrides. Although it is now generally accepted that the hydrogen is directly bonded to the metal, there is a paucity of direct experimental evidence about metal–hydrogen (M–H) bond distances in molecules of this type. Values for the M–H bond distance ranging from 1.0–1.2[1–6] to 1.4–2.0 A[7–11] have been suggested. Manganese carbonyl hydride is especially amenable to a broad-line proton nmr study since manganese-55 has a large spin quantum number and a large magnetogyric ratio and is 100% abundant. The situation is

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(1) F. A. Cotton and G. Wilkinson, *Chem. Ind.* (London), 1305 (1956).

(2) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

(3) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

(4) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *ibid.*, 2484 (1959).

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(6) M. Gerlock and R. Mason, *ibid.*, 296 (1965).

(7) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, 3, 22 (1964).

(8) W. F. Edgell, C. Magee, and G. Gallup, *J. Am. Chem. Soc.*, 78, 4185 (1956); W. F. Edgell and G. Gallup, *ibid.*, 78, 4188 (1956).

(9) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, 3, 1495 (1964).

(10) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3502 (1963).

(11) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 3, 558 (1964).

even more favorable since LaPlaca, Hamilton, and Ibers[9] have determined all of the structural parameters except the position of the hydrogen. They have shown, in agreement with infrared[12] and Raman[13] studies, that $HMn(CO)_5$ has C_{4v} symmetry and that pairs of $HMn(CO)_5$ molecules are oriented such that their C_{4v} symmetry axes intersect with a 135° angle and that the distance between the two manganese atoms is 5.167 A. They assume that the hydrogens lie on the C_{4v} symmetry axes and on the basis of this assumption they obtained the relation

$$r_{\text{Mn-H}} = 2.804 - 0.543 r_{\text{H-H}} \qquad (1)$$

where the distances are expressed in angstroms, $r_{\text{Mn-H}}$ is the intramolecular Mn-H bond distance, and $r_{\text{H-H}}$ is the intermolecular H-H distance.

It follows from the work of Van Vleck[14] that the second moment, ΔH_2^2, of the proton nmr absorption spectrum of a polycrystalline sample of $HMn(CO)_5$ can be written as

$$\Delta H_2^2 = 358.071 r^{-6}_{\text{H-H}} + 114.064[r^{-6}_{\text{Mn-H, inter}} + r^{-6}_{\text{Mn-H, intra}}] \qquad (2)$$

The $r_{\text{H-H}}$ term of eq 2 arises from the intermolecular H-H interaction. The second and third terms arise from the inter- and intramolecular Mn-H interactions, respectively. The intermolecular Mn-H interaction accounts for less than 0.5% of the contribution to ΔH_2^2 and can be neglected. From eq 1 and 2 one can obtain an equation expressing $r_{\text{Mn-H}}$ as a function of ΔH_2^2; the equation has two real roots.

A value of 26.6 ± 0.6 G^2 {10^4 gauss (G) = 1 tesla (T)}[15] was determined for the second moment (this value was corrected for modulation broadening[16]) of a carefully purified[17] polycrystalline sample at −165°. This value for ΔH_2^2 corresponds to Mn-H distances of 1.281 or 1.950 ± 0.02 A. By eq 1, the longer distance gives an intermolecular H-H distance of 1.57 A, which is much less than the normal van der Waals contact of 2.2 A[10] and is therefore extremely unlikely. Furthermore, since (see eq 2) the intramolecular Mn-H interaction accounts for more than 97% of the observed value of ΔH_2^2, our result does not depend upon the validity of the assumption that the hydrogens lie along the C_{4v} symmetry axes.[18]

Further studies of other transition metal carbonyl hydrides are in progress.

Acknowledgments. This work was supported in part by National Science Foundation Grant GP-3468.

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(12) H. D. Kaesz and D. K. Huggins, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

(13) A. Davison and J. W. Faller, to be published.

(14) J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).

(15) All of the errors reported here are average errors: see, for example, H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 1st ed, D. Van Nostrand Co., New York, N. Y., 1943, p 493.

(16) This value has not been corrected for zero point vibration. This correction, however, will not change the value of ΔH_2^2 by more than 2 or 3% and would change the value of the Mn-H bond distance by less that 1%. ΔH_2^2 was obtained by integrating the proton nmr absorption spectrum over a 40-gauss interval centered about the absorption maximum.

(17) No impurities were observed in microwave, infrared, or high-resolution proton nmr spectra. The value for ΔH_2^2 is virtually constant from about −40 to −165°.

(18) Even in the Mn-H bond distance range 1.5-1.6 A, where ΔH_2^2 = 11.95 to 9.91 gauss^2, the Mn-H dipole-dipole contribution to ΔH_2^2 is very large (84 to 69%).

(19) Participant in National Science Foundation Chemistry-Physics Teacher Institute, summer 1965.

(20) National Science Foundation Predoctoral Fellow, 1963-1966.

Thomas C. Farrar, Sr. W. Ryan[19]
National Bureau of Standards
Washington, D. C. 20234

Alan Davison, J. W. Faller[20]
Department of Chemistry,
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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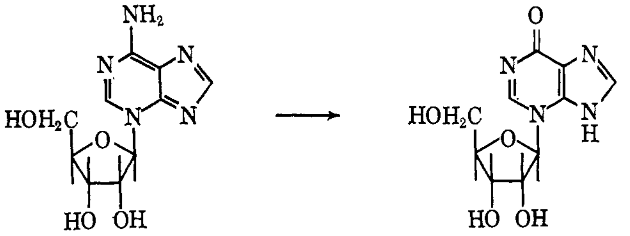
Enzymatic and Chemical Deamination of 3-(β-D-Ribofuranosyl)adenine[1]

Sir:

3-Isoinosine (3-(β-D-ribofuranosyl)hypoxanthine) (II) has been prepared from 3-isoadenosine (3-(β-D-ribofuranosyl)adenine) (I)[2] in our two laboratories by enzymatic and chemical procedures, respectively. The deamination of isoadenosine by an adenosine deaminase from *Aspergillus oryzae*, unexpected in view of the somewhat altered electronic configuration of the purine ring, renders less likely one mechanism for the action of the enzyme on adenosine. The independent chemical synthesis of isoinosine, which presents unusual requirements because of the lability of the N_3-C_1' bond, made possible direct identification of the enzymatic product.



I

II

The adenosine deaminase of *Aspergillus oryzae*[3] has been purified approximately 5000-fold by methods which will be described in a subsequent communication.[4] The purified enzyme shows no ultraviolet absorption maxima above 300 mμ. Its activity is unaffected by the presence of 0.001 *M* ethylenediaminetetraacetic acid or by dialysis against neutral phosphate buffer, and it is not detectably inhibited by 0.001 *M* hydrazine or 0.05 *M* cysteine, suggesting that pyridoxal is not a cofactor. A mechanism for deamination of adenosine, not requiring Schiff base formation with the enzyme or cofactors, would involve protonation by the enzyme of the purine ring at N_1 or N_3, shifting adenosine to its 6-imino tautomer and potentially facilitating hydrolysis. It was of particular interest to test the possible activity of the deaminase on 3-isoaden-

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(1) The work at Princeton University was supported by Research Grant USPHS-GM-12725 from the National Institute of Health, U. S. Public Health Service. The work at the University of Illinois was supported by Research Grant USPHS-GM-05829-06/07) from the National Institutes of Health, U. S. Public Health Service.

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(3) H. K. Mitchell and W. D. McElroy, *Arch. Biochem.*, **10**, 351 (1946); T. P. Wang and N. O. Kaplan, *J. Biol. Chem.*, **206**, 311 (1954).

(4) T. K. Sharpless and R. Wolfenden, in preparation.