ized as a $({}_{\pi}2_s + {}_{\pi}2_a)$ adduct of TCNE onto cis^2,*trans*,-*cis*-CNT (**13**).[25] In closing, it would be instructive to contrast the thermal behavior of **1** with that of its 9,9-dialkyl analogs. The recently established[4] propensity of the latter to thermally rearrange by way of a *gem*-9,9-dialkyl cis^3,*trans*-CNT intermediate when considered together with their obvious steric inability to assume a "folded" conformation[4] necessary for a "Cope" rearrangement and the uncommonly high temperature they require for thermolysis[26] clearly suggests that *given a choice, a cis-bicyclo*[*6.1.0*]*nona-2,4,6-triene will rearrange through a "Cope" process and that symmetry-controlled rupture of the cross-link would set in as a serious mechanistic competitor only in the event the "Cope" rearrangement is seriously obstructed.* Trapping experiments involving certain select substituted bicyclo[6.1.0]nonatrienes, currently in progress within our laboratories, would hopefully provide a basis for firm generalization of the above statement.

Acknowledgment. Support of this work by the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged. We also wish to thank Drs. H. E. Simmons and T. Fukunaga and Mr. L. Rizzardi for supplying us with the 220-MHz nmr spectra.

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[25] Of course, this statement is strictly applicable only in the event the bicyclic TCNE cycloadduct in question is cis fused. Unfortunately, the detailed stereochemistry of the TCNE cycloadduct appears not to be known.[23,24]

[26] Upon monitoring the thermal rearrangement of **1** by nmr spectroscopy at three different temperatures we obtain $\Delta H^{\ddagger} = 26$ kcal/mol and $\Delta S^{\ddagger} = -5$ eu. Using these values in conjunction with data recorded by Staley and Henry[4] on the thermal rearrangement of 9,9-dimethyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene we estimate that at 151° this latter substance is characterized by a $\Delta F^{\ddagger}$ term which is *ca.* 4 kcal/mol higher than that of **1**.

[27] National Science Foundation Graduate Trainee, 1969–present.

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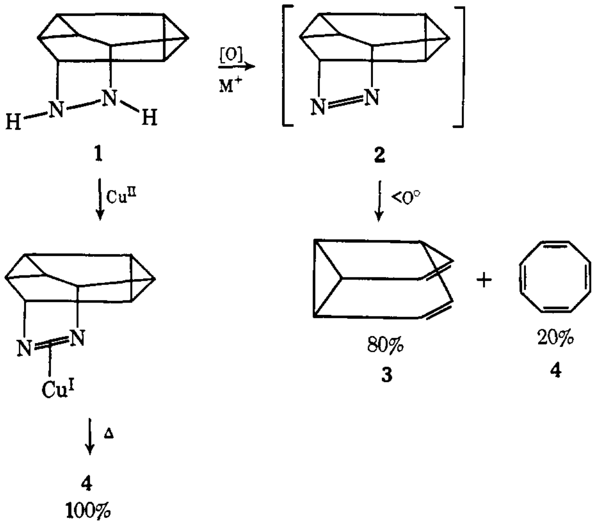
Thermolysis of 7,8-Diazapentacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,9}]dec-7-ene. Effect of Transition Metal Ions upon the Formation of Semibullvalene and Cyclooctatetraene

Sir:

Recently Paquette[1] and Askani[2] reported the synthesis and thermal decomposition of 7,8-diazapentacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,9}]dec-7-ene (**2**) to yield semibullvalene (**3**) as the sole volatile product. In our investigation of this same problem we found that cyclooctatetraene was invariably a minor coproduct and its occurrence amounted to 5–20% depending upon the method of oxidation of hydrazine **1**.

Oxidation of hydrazine **1**[3] with mercuric oxide, manganese dioxide, or cupric chloride in various solvents yielded a reproducible ratio of semibullvalene to cyclooctatetraene of 80:20%. Paquette used mild air oxidation for reaction **1** → **2**. This suggested the possibility that the discrepancy between our results might be due to a transition metal catalyzed conversion of semibullvalene (**3**) to cyclooctatetraene (**4**). Indeed this was found to be the case. Transition metals catalyze the quantitative rearrangement of **3** to **4**.[4] However, the important question remained of whether the metal-catalyzed decomposition of **2** occurs to yield **4**. Toward elucidating this point the thermal decomposition of the copper complex of **2** was studied. The Cu(I) complex of **2**[5] was decomposed at 25° as a pure solid. Cyclooctatetraene was obtained as the only organic product.



The facile thermal loss of nitrogen from **2** to yield **3** is the reverse of an allowed homoconjugate Diels–Alder cycloaddition. As pointed out by Paquette, the reaction is favored on the basis of orbital symmetry, molecular geometry, and strain.

We believe that the metal-catalyzed formation of cyclooctatetraene (**3**) and nitrogen results from a competing concerted retroelectrocyclization which becomes the sole pathway in the decomposition of the Cu(I) complex of **2**. This belief is based upon the following analysis. If one considers the transition state for the reverse process, namely, the hypothetical cycloaddition of nitrogen to cyclooctatetraene, it is recognized as containing 10π electrons. It is a $4n + 2$ system and the thermal electrocyclization is favored by electron delocalization in the aromatic transition state. Although it may not immediately be apparent, the array of ten 2p atomic orbitals may be placed on a closed loop as shown in **5**.

In this sense the transition state is isoconjugate with cyclodecapentaene. Structures **6** and **7**, in which arbitrary basis sets are selected for the 2p atomic orbitals, illustrate these relationships. Note that in each either zero or an even number of sign inversions occur; *i.e.* **6** has zero sign inversions and **7** has four.[6]

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[1] L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5766 (1970).

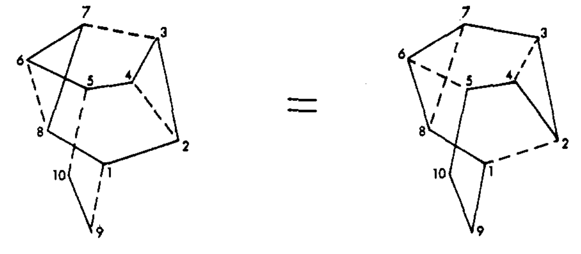
[2] R. Askani, *Tetrahedron Lett.*, **38**, 3349 (1970).

[3] Either the dimethyl or diethyl ester of diazabasketane underwent rearrangement with $CH_3OH \cdot H_2O$ (3:1), $AgNO_3$ with reflux for 24 hr to the diaza esters in 80% yield. The diethyl ester has bp 155–156° (0.30 mm); nmr ($CDCl_3$, ppm) 5.03 (2 H, m, NC*H*); 4.25 (4 H, q, J = 7 Hz, OCH_2–), 1.95 (6 H, m, cyclopropyl), 1.30 (6 H, t, J = 7 Hz, $-CH_3$). The dimethyl ester had mp 130–131°, and the nmr was similar to the diethyl ester. Hydrazine (**1**) was obtained by base treatment of the diester: 3.80 (2 H, m, HCCN), 3.45 (2 H, s, *H*N), 1.77 (6 H, m, cyclopropyl).

[4] Details will be reported separately. Typically silver nitrate at 80° for 24 hr in aqueous methanol effects the conversion. A stable silver nitrate complex of semibullvalene was also obtained with composition $C_8H_8AgNO_3$, mp 87° dec. Semibullvalene could be recovered from this complex. The iron carbonyl, palladium, and platinum complexes were also formed.

[5] This complex, 2-CuCl, had mp 95–96° dec and was prepared by oxidation of **1** with $Cu^{II}Cl_2$.

[6] H. E. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).



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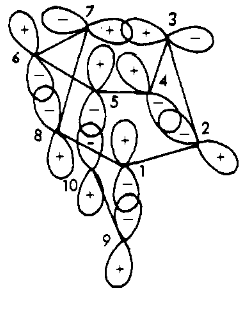

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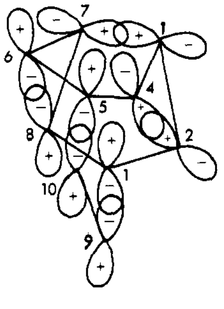

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The overlap of the 2p atomic orbitals is in phase for formation of the potential σ bonds and the movement about the C_1–C_8, C_5–C_6, and C_1–C_2 and C_4–C_5 bonds is inwardly disrotatory. The cycloaddition may also be described as a ${}_{\pi}2_a + {}_{\pi}2_a + {}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ formation of the C_6–C_8, C_7–C_3, and C_4–C_2 bonds occurring in the antara manner.[7] Bonding of the azo group to Cu(I) does not change the occupancy of the atomic orbitals but does lower the energy of activation for the alternative retroelectrocyclization to yield cyclooctatetraene and nitrogen.

Now it should be recognized that the forward reaction, namely, the Diels–Alder cycloaddition of a 2π system to cyclooctatetraene, cannot give an analog to **2**. This is because Diels–Alder adducts usually derive from the bicyclo[4.2.0]octa-2,4,7-triene valence tautomer.[8,9] We argue that even though formation of an adduct analogous to **2** is thermally allowed, the reaction between the 2π dienophile takes precedence. However, the present example, $\mathbf{2} \rightarrow \mathbf{4} + N_2$, represents the allowed reverse of this hypothetical reaction. An interesting corollary of this interpretation is that metal complexation of the azodienophile in reaction with cyclooctatetraene should yield an adduct analogous to **2**. This point is under investigation.

Acknowledgment. The authors wish to thank Professor D. G. Gorenstein of this department and Professor H. E. Zimmermann, University of Wisconsin, for helpful discussions.

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[7] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

[8] R. Huisgen and F. Mietzsch, *ibid.*, 3, 83 (1964).

[9] For examples in which COT reacts directly in the Diels–Alder reaction see: A. B. Evin, R. D. Miller, and G. R. Evanega, *Tetrahedron Lett.*, 5863 (1968); E. Vedejs and R. A. Shepherd, *ibid.*, 1863 (1970).

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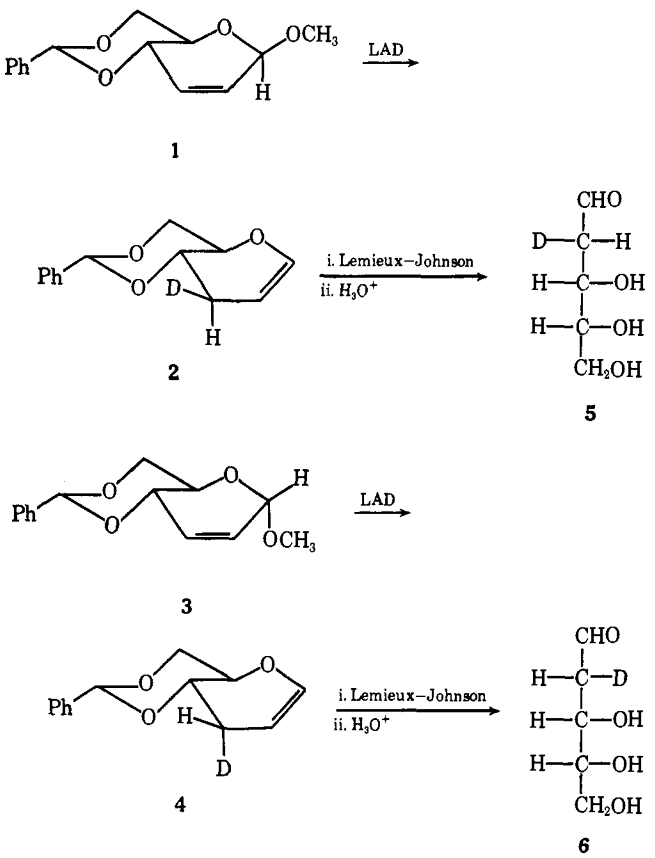
The Specifically 2-Monodeuterated 2-Deoxy-D-riboses (2(*S*)- and 2(*R*)-Deuterio-2-deoxy-D-erythropentoses)

Sir:

A recent report from this laboratory described the completely stereospecific production of the deuterated glycals **2** and **4** from acetals **1** and **3**, respectively.[1] We now report that the 2-monodeuterated 2-deoxy-D-riboses, 2(*S*)- and 2(*R*)-deuterio-2-deoxy-D-erythropentoses, **5** and **6**, respectively, are readily obtainable from **2** and **4** *via* cleavage of the olefin and subsequent debenzylidenation, with complete retention of stereospecificity of the label.



Lemieux–Johnson oxidation[2] of glycal **2** (219 mg; 1.0 mmol) dissolved in 16 ml of dioxane–water (3:1) mixture using osmium tetroxide (2×10^{-2} mmol)[3] and sodium metaperiodate (1.07 g; 5 mmol) was complete (tlc) in 0.5 hr. The excess periodate was destroyed with ethylene glycol and the product recovered by extraction into ether.[4] The semicrystalline residue was treated for 1.5 hr with dilute sulfuric acid and the neutralized aqueous layer freed from benzaldehyde by chloroform extraction. The deuterated sugar, **5**, was present in the syrup obtained upon evaporation of the

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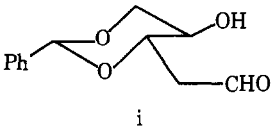
[1] B. Fraser-Reid and B. Radatus, *J. Amer. Chem. Soc.*, **92**, 6661 (1970).

[2] R. Pappo, D. S. Allen, R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

[3] Added as 1 ml of a solution of 0.1 g of OsO_4 in 20 ml of *tert*-BuOH.

[4] The Lemieux–Johnson oxidation product from the ^1H analog of 2[1] was on occasion isolated and shown to be i by spectral data and



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microanalysis of the derived semicarbazone.