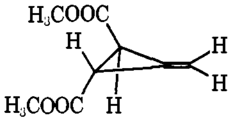
currence of **4** as a stable intermediate in the reaction, provided that it has the open shell singlet structure (S$_1$). On this basis the predominant formation of **6** rather than **7** from **5** must presumably be attributed to steric effects, because the transition states leading from **5** to **6** or **7** should be equally favorable on electronic grounds, both being nonaromatic.[6,15]



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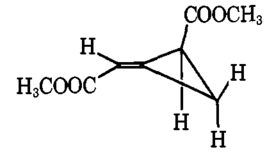

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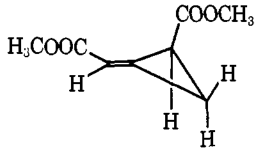

7

The next step will be a detailed study of the reaction path leading from methylenecyclopropane to **2** and the effect of substituents on it. However, the results reported here seem sufficient to make any concerted mechanism unlikely, as would be expected since the geometry of the intermediate **2** is such as to inhibit effective overlap between the atomic orbitals of the methylene groups.

(15) M. J. S. Dewar, *Angew. Chem.*, in press.

Michael J. S. Dewar,* John S. Wasson
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

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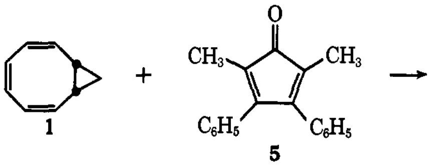
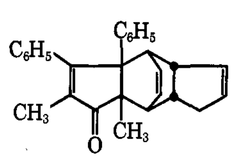
Evidence for *cis,cis,trans,cis*-1,3,5,7-Cyclononatetraene in the Thermal Bond Relocation of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene

Sir:

The details of the thermal reorganization of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) to *cis*-8,9-dihydroindene (**2**)[1] have been the subject of intense activity.[2-6] Concern over the nature of this rearrangement derives chiefly from the fact that while disallowed on the basis of orbital symmetry, its activation requires only mild heating. It was pointed out,[3] for example, that thermal rupture of the cross-link in **1** should occur conrotatorily to generate *cis,cis,cis,trans*-1,3,5,7-cyclononatetraene (*cis*^{3},*trans*-CNT) (**3**) which, in turn, ought to electrocyclize disrotatorily to trans- rather than the observed cis-fused 8,9-dihydroindene. Interestingly, this prediction was recently substantiated in full in the case of two 9,9-dialkyl derivatives of **1** both of which were shown to produce chiefly *trans*-8,9-dihydroindene skeletons on thermolysis.[4] Further, the case for strict orbital-symmetry control within these systems was strengthened considerably by the recent observation[7-10] that thermolysis of *all-cis*-CNT (**4**) does indeed lead to the expected cis-fused 8,9-dihydroindene (**2**). Presently, we record results of key trapping experiments which, we believe, have direct bearing on the mechanistic details of the thermolysis of **1**.



A(25%) + B(45%) + C(30%)



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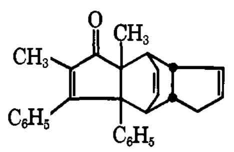

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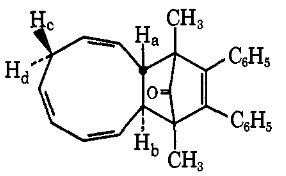

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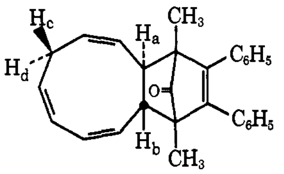

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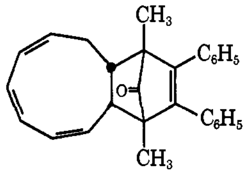

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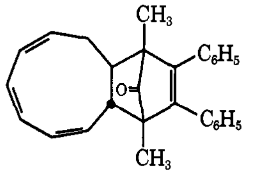

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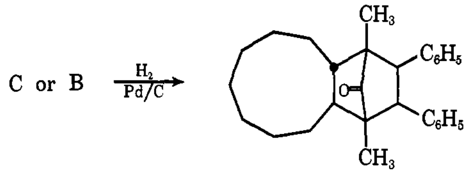

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Treatment of **1** with an equimolar quantity of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (**5**)[11] in boiling benzene led, cleanly and quantitatively, to three 1:1 adducts:[12,13] **A** (25%) [white needles, mp 220–220.5°; $\nu_{\mathrm{CO}}^{\mathrm{KBr}}$ 1675 cm^{-1}; *m/e* 378 (P$^+$; 10%); nmr (60 MHz; CDCl$_3$) multiplets at τ 2.6–3.0 (8 H), 3.4–3.7 (2 H), 3.9–4.1 (2 H), 4.4–4.7 (2 H), 6.3–8.2 (6 H), and sharp singlets at 8.30 (3 H) and 8.90 (3 H)]; **B** (45%) [white crystals; mp 132–133°; $\nu_{\mathrm{CO}}^{\mathrm{KBr}}$ 1760 cm^{-1}; *m/e* 378 (P$^+$; 23%); nmr (60 MHz; CDCl$_3$) multiplets at τ 2.7–3.2 (10 H), 3.8–4.7 (6 H), 7.0–7.8 (4 H), and sharp singlets at 8.62 (3 H) and 8.83 (3 H)]; and **C** (30%) [white plates; mp 127–128°; $\nu_{\mathrm{CO}}^{\mathrm{KBr}}$ 1760 cm^{-1}; *m/e* 378 (P$^+$; 31%); nmr (60 MHz; CDCl$_3$) multiplets

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(1) E. Vogel, *Angew. Chem.*, **73**, 548 (1961); **74**, 829 (1962).

(2) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(3) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968).

(4) S. W. Staley and T. J. Henry, *ibid.*, **91**, 1239, 7787 (1969).

(5) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969).

(6) J. C. Barborak, T. -M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *ibid.*, **93**, 279 (1971).

(7) G. Boche, H. Boehme, and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **8**, 594 (1969).

(8) P. Radlick and G. Alford, *J. Amer. Chem. Soc.*, **91**, 6529 (1969).

(9) A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969).

(10) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

(11) C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942); **72**, 5165 (1950).

(12) The adducts are stable to prolonged heating at the reaction temperature.

(13) Correct elemental analysis was obtained for all new compounds reported.

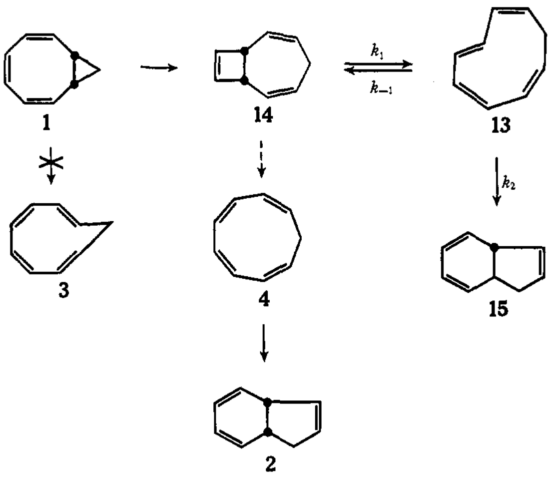
at τ 2.6–3.2 (10 H), 3.8–4.7 (6 H), τ 7.1–7.9 (4 H), and sharp singlets at 8.72 (3 H) and 8.78 (3 H)].

Clearly, the magnitude of ν_{CO} within A suggests the presence of an α,β-unsaturated carbonyl function, while the presence of four "olefinic" and six "aliphatic" protons firmly implicates a bicyclic hydrocarbon segment. Finally, this substance was isolated as the sole product in the reaction of *cis*-8,9-dihydroindene with **5** at 80°. All available information, spectral and chemical, thus serves to formulate A as either **6** or **7**, *i.e.*, a ($_{\pi}2_s + {}_{\pi}4_s$) product of **2** and **5** with the latter furnishing the $_{\pi}2_s$ segment. The spectral data on B and C clearly require the presence of (1) a highly strained ketonic function (ν_{CO}) and (2) a monocyclic hydrocarbon segment (nmr). Furthermore, the appearance, in each case, of two distinct methyl signals in the nmr spectrum demands that the adducts in question possess an unsymmetrical hydrocarbon moiety.[14] Further, prolonged catalytic (Pd/C) hydrogenation of either B or C produced a single $C_{28}H_{34}O$ substance **8** [mp 141–142°; ν_{CO}^{KBr} 1750 cm^{-1}; *m/e* 386 (P$^+$; 37%); nmr (60 MHz; $CDCl_3$) multiplets at τ 2.7–3.2 (10 H), 7.0–7.6 (2 H), 7.8–9.0 (20 H), and singlets at 6.33 (2 H), 8.73 (3 H), and 8.84 (3 H)]. The formation of the same hydrogenated product from either B or C clearly implicates a cyclononane segment within this compound, while the presence of two distinct methyl resonances in its nmr spectrum requires that this segment be fused trans to the remainder of the molecule. That this is in fact the case was firmly established through synthesis of **8** (nmr, ir, mixture melting point) from the reaction of **5** with *trans*-cyclononene[15] at 80° followed by prolonged catalytic (Pd/C) hydrogenation. This information effectively limits the structural possibilities for B and C to those formulated in **9**, **10**, **11**, and **12**.

Proper selection of the correct structures for B and C necessitated extensive nmr analysis at 100 and 220 MHz[16] along with selective deuterium labeling.[17] The results obtained along these lines[18] served to effectively single out structures **9** and **10** for the two cycloadducts under discussion, on account that *neither in B nor in C are the methylene hydrogens coupled to either of the two methine protons.*[19] Finally, comparison of the 100 MHz (or 220 MHz) nmr spectrum of B and C taken in $CDCl_3$ provides a rational basis for specific structural assignments. In brief, the two spectra differ most obviously with regard to the relative position of the methine hydrogens. In B these exhibit identical chemical shifts while in C they appear well separated owing to a shift of one methine resonance to substantially higher field. Careful inspection of "Dreiding" molecular models of **9** and **10** reveals that the endo methine proton of **9** (H$_b$) best accounts for the observed upfield shift for it is uniquely located quite close (~2.3 Å) to the shielding portion of an olefinic function. Therefore, we tentatively propose that B and C are **10** and **9**, respectively.

In terms of mechanism, **9** and **10** are most reasonably viewed as thermally allowed ($_{\pi}2_s + {}_{\pi}4_s$) products of **5** and *cis*^{2},*trans*,*cis*-CNT (**13**), the formation of two stereoisomeric adducts clearly reflecting the asymmetry imparted to the hydrocarbon **13** by the trans double bond.[20] The most likely source of **13** is of course *cis*-bicyclo[5.2.0]nona-1,4,7-triene (**14**) which could formally generate the monocycle in question through symmetry-allowed conrotatory rupture of its cross-link. In turn, **14** ought to be readily accessible from **1** by way of a similarly allowed thermal process, *i.e.*, a 3,3-sigmatropic ("Cope") rearrangement. Finally, the complete absence of adducts **11** and **12** among the reaction products effectively discounts the much conjectured intermediacy of *cis*^{3},*trans*-CNT (**3**) in the thermal reorganization of **1** to **2**.[21] In brief, we believe our present results to be rationally and perhaps uniquely accommodated by the set of transformations collected in Scheme I in which we depict symmetry-allowed and symmetry-forbidden steps by solid and dashed arrows, respectively.[22] Within the frame of the proposed mechanism, formation of cis-fused 8,9-dihydroindene (**2**) on thermolysis of **1** is best reasoned in terms of a pronounced kinetic inequality, *i.e.*, $k_{-1} \gg k_2$, which ought to allow for eventual drain of **14** into *all-cis*-CNT (**4**), a well-documented[7–10] thermal precursor of **2**. It is also interesting to note in this connection that the results of our trapping experiments are entirely in keeping with those of related experiments by other workers[23,24] whereby **1** was thermolyzed in the presence of tetracyanoethylene (TCNE) to yield a bicyclic adduct which, in our judgment, is best rational-

Scheme I



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(14) We note in this connection that the presence in these compounds of a bridge carbonyl group requires that the segment of the adduct due to **5** be symmetrical. Hence, the overall lack of symmetry within these substances must be due to the hydrocarbon segment.

(15) A. C. Cope, D. C. McLean, and N. A. Nelson, *J. Amer. Chem. Soc.*, 77, 1628 (1955).

(16) We thank Mr. L. Rizzardi for the 220-MHz nmr spectra.

(17) B-d_2 and C-d_2 specifically labeled at the methylene function were prepared from **5** and 9,9-dideuterio-*cis*-bicyclo[6.1.0]nona-2,4,6-triene.

(18) At the suggestion of a referee we deleted the details of this nmr study which were supplied in full in the original version of the manuscript.

(19) Careful analysis of the nmr spectra allows for a consistent assignment of *all* coupling constants. These will be recorded in the full paper.

(20) In principle, of course, structures such as **9** and **10** could materialize directly from **1** and **5**. In practice, we believe this to be unlikely on account of the pronounced regiospecificity as well as stereospecificity characterizing this reaction.

(21) Significantly, the presence of deuterium exclusively within the methylene functions of **9**-d_2 and **10**-d_2 establishes beyond doubt that these substances do not arise by way of their position isomers, **11** and **12**, since any hydrogen shift(s) necessary to effect such a transformation will necessarily scramble the label.

(22) It is instructive to note here that a scheme akin to but less specific than that depicted here in I was recently considered by other workers[5] on a purely speculative basis.

(23) W. H. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1970).

(24) C. S. Baxter and P. J. Garratt, *ibid.*, **92**, 1062 (1970).

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.

A. G. Anastassiou,* R. C. Griffith[27]
Department of Chemistry, Syracuse University
Syracuse, New York 13210

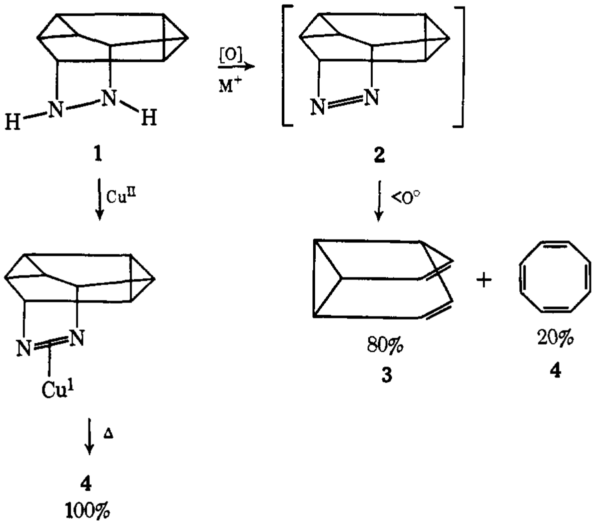
Received February 9, 1971

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).