EWG acids, based on a pK of 50 for methane,[9] are compared with those of phenols.

Examination of Table II shows that, as would be expected, the acidifying effects of EWG are greatly exaggerated when it is attached directly at the acidic site (CH₃EWG) instead of across a benzene ring. Note, for example, that a p-NO₂ group enhances the acidity of phenol in DMSO by ca. 6 pK units, whereas the effect on methane is 35 or more pK units, depending on the pK assigned to methane.[9,12] The relative order of effects remains essentially the same, however, i.e., $NO_2 > CH_3CO > CH_3SO_2$, CN, which is the order expected if the stronger delocalizing effect of CH_3CO, relative to CH_3SO_2 or CN, overrides its much weaker inductive effect (σ_{R^-} for CH_3CO is 0.47 compared to 0.38 and 0.33 for CH_3SO_2 and CN; the corresponding σ_I values are 0.28, 0.59, and 0.56[13]).

The magnitude of the $\Delta p K$ values for the methane series is impressive. The estimated minimum increase in acidity of 35 pK units on substitution of a nitro group for a hydrogen atom of methane corresponds to 48 kcal/mol of stabilization energy in the resulting anion.

(9) Estimates of the pK of methane range from 40 to 84.[10] A linear extrapolation from $CH_2(CN)_2$ (pK 11.0 in DMSO[4]) to CH_3CN (pK 29.1 in DMSO (Table I)) to CH_4 gives a pK of 47 for methane. It seems likely, however, that $\Delta p K$ for the change from CH_3CN to CH_4 is much larger than that from $CH_2(CN)_2$ to CH_3CN. The value of 47 also appears to be too low based on an estimated pK of benzene as ca. 49 in DMSO. The latter estimate is based on Streitwieser's extrapolated value of 43 for benzene in CHA.[11] Since we find that the pK of phenylacetylene,[1b] a carbon acid forming a localized carbanion similar to that obtained from benzene, is ca. 6 units higher in DMSO than in CHA, an increment at least as large can be assumed for benzene. A pK of 50 for methane in DMSO appears minimal from these considerations, and a considerably higher value, say 60, does not appear unreasonable.
(10) See (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter I; (b) A. Streitwieser, Jr., W. C. Langworthy, and J. J. Brauman, *J. Amer. Chem. Soc.*, **85**, 1761 (1963).
(11) A. Streitwieser, Jr., P. J. Scannon, and H. H. Neimeyer, *J. Amer. Chem. Soc.*, **94**, 7936 (1972).
(12) A single p-NO₂ group increases the acidity of triphenylmethane in DMSO by ca. 12 pK units.[7]
(13) S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 9113 (1972).
(14) National Science Science Foundation Postdoctoral Fellow, 1971–1972.

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deuterium labeling studies and other experiments have implicated an intramolecular $(4 + 2)\pi$ cycloaddition pathway for these rearrangements and subsequent valence isomerization (if suprafacial, symmetry allowed) of the cis^2-bishomobenzene intermediates, **2**.

$\underset{\sim}{1} \qquad \underset{\sim}{2} \qquad \underset{\sim}{3}$

$\underset{\sim}{a}$, n = 2 ; $\underset{\sim}{b}$, n = 3

The marked preference for the Diels–Alder bishomoconjugative mechanism in such systems is further reflected specifically in the thermal self-interconversions of cyclooctatetraenes[2] and, less categorically, in the behavior of a wide array of [4.2.2] and [4.2.1] bicyclic structures.[3] We have considered the possibility that this interesting pathway, requiring as it does the involvement of all six pπ electrons in **1**, could be blockaded and perhaps redirected in the presence of a transition metal. Such an alternate bond reorganization pathway has been observed and forms the subject of this report.

When **1a** was heated at reflux with 30 mol % Mo(CO)₆ (freshly sublimed) in anhydrous benzene under a purified nitrogen atmosphere for 36 hr, isomerization to **3a** (41% isolated[4]) was observed. Control experiments involving the heating of **1a** in refluxing benzene for >2 days resulted in total recovery of unchanged propellane. In contrast, reaction of **1a** with the more reactive Mo(CO)₃(diglyme)₃ reagent[5] in diglyme–benzene (10:3) at 25° for 18 hr led to formation of complex **4a** (43%), obtained as pale yellow crystals, mp 90–92° (from pentane). The nmr spectrum of **4a** [δ(CDCl₃) 5.57 (s, 2 H), 4.69 (s, 2 H), 4.60 (s, 2 H), 2.4–2.0 (m, 4 H), and 1.1–1.75 (m, 4 H)] suggested complexation of molybdenum to 1,5-olefinic groups in the bicyclic valence isomer as expected of the specific geometrical requirements of the coordinated Mo(CO)₄ moiety.[6] This conclusion was confirmed and the complete stereochemistry of the complex revealed by three-dimensional X-ray crystal structure analysis (Figure 1).

Systematic extinctions uniquely required the space group $P2_1/n$ (C_{2h}^5-alternate setting) with four molecules in a unit cell of dimensions $a = 17.962$ (5), $b = 11.944$ (3), $c = 7.125$ (2) Å, and $\beta = 93.65$ (2)°. All crystals that were examined were polysynthetic twins in which
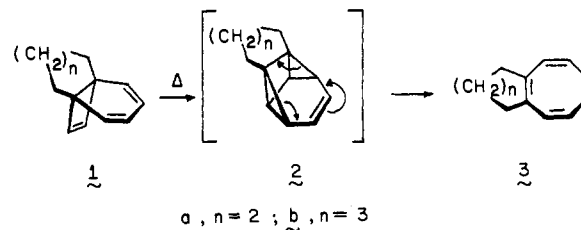
Transition Metal Promoted Redirection of the Thermal Bishomoconjugative Bond Reorganization Pathway of Unsaturated Propellanes

Sir:

Thermolysis of tricyclic [4.2.0]octatrienes of general formula **1** above 400° in the gas phase (contact times of 1–3 sec) is recognized not to involve aromatization with loss of acetylene (symmetry disallowed) but rather to proceed with formation of the structurally isomeric cyclooctatetraenes, **3**, in good yields.[1] Appropriate

(1) L. A. Paquette and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 4398 (1972).

(2) (a) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 9224 (1972); (b) L. A. Paquette and M. Oku, *ibid.*, **96**, 1219 (1974).
(3) (a) W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg, and M. B. Rubin, *Helv. Chim. Acta*, **53**, 725 (1970); (b) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **95**, 2230 (1973); (c) M. J. Goldstein and S. A. Kline, *Tetrahedron Lett.*, 1089 (1973), and references contained in these papers.
(4) This rearrangement was accompanied by the formation of significant amounts of dark intractable material.
(5) T. H. Coffield and R. P. M. Werner, U. S. Patent 3,124,600; *Chem. Abstr.*, **60**, 15914 (1964); R. P. M. Werner and T. H. Coffield, *Chem. Ind. (London)*, 936 (1960).
(6) For earlier examples see (a) E. O. Fischer and W. Frölich, *Chem. Ber.*, **92**, 2995 (1959); (b) M. A. Bennett and G. Wilkinson, *Chem. Ind. (London)*, 1516 (1959); (c) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Amer. Chem. Soc.*, **88**, 1319 (1966); Y. Menachem and A. Eisenstadt, *J. Organometal. Chem.*, **33**, C29 (1971).
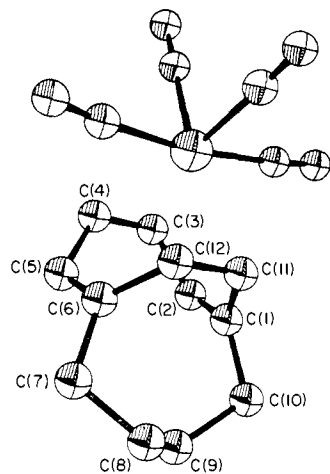
Figure 1.

b^* and a^* of the mates were colinear. Thus, all reflections of the type $hk3n$ contained contributions from each mate according to the relation

$$I(h,k,3n) = [KI_{obsd}(-h-n,k,3n) - I_{obsd}(h,k,3n)]/(K^2 - 1)$$

where I_{obsd} is the observed intensity at a reciprocal lattice point and K is a scale factor obtained from nonoverlapping reflections. A total of 2410 independent reflections with $\theta \leq 62°$ were collected with a diffractometer using Cu Kα radiation (1.5418 Å). After correction for Lorentz, polarization, background, and twinning effects, 1477 reflections with $F_o \geq 3\sigma(F_o)$ were judged observed. Full-matrix least-squares refinements rapidly converged to the present discrepancy index of 0.077.[7] The molecule is characterized by a noncrystallographic approximate mirror plane that is broken only by atoms C(8) and C(9). The complexed double bonds are significantly longer than the noncomplexed double bonds (1.39 vs. 1.35 Å). The distance between atoms C(1) and C(6) is 2.77 Å.

Unlike cyclooctatetraenemolybdenum tetracarbonyl which tends to disproportionate readily with loss of CO,[6c] complex **4a** exhibits good shelf-life stability. This reluctance to disproportionate likely resides in the inability (due to annulation) of the unsaturated ligands to provide a nearly planar conjugated 1,3,5-triene segment required for hexahapto bonding to Mo(CO)$_3$. Under conditions where hydrocarbon **1a** experienced rearrangement, **4a** underwent partial (35%) degradation to give **3a** in low yield. With added Mo(CO)$_6$, however, the conversion to **3a** proceeded to high (82% isolated) conversion. Consequently, the possibility remains open that tetrahapto complex **4a** is a transient intermediate in the isomerization of **1a**.

For the purpose of mapping the course of rearrangement, **1a**-*11,12-d$_2$*[1] was prepared and similarly treated with Mo(CO)$_6$ in refluxing benzene. The resulting 1,2-annulated cyclooctatetraene was not isolated but converted directly to its TCNE adduct **6a**, the three proton pairs of consequence in which have previously been

5 **6**

$\underline{a}$, n = 2 ; $\underline{b}$, n = 3
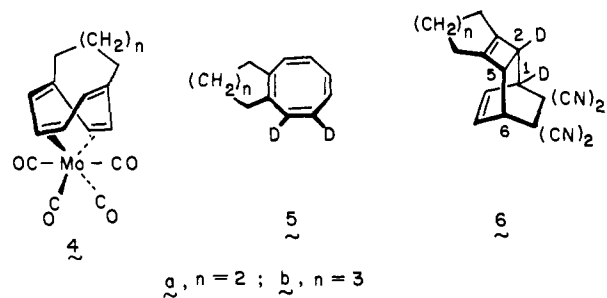
shown to exhibit distinctly different chemical shifts.[8] The nmr spectrum revealed the absence of one proton each from the cyclobutane and bridgehead areas. The 1,2 (as opposed to 1,5) relationship of the deuterium atoms in the adduct was established by LAOCOON III simulation of the 100-MHz spectrum.[9] The unique isolation of **6a** defines the rearrangement as consisting formally of a 1,5 sigmatropic cyclobutene shift, in clear contradistinction to the purely thermal reaction channel.[1]

When heated with Mo(CO)$_6$ in benzene for 17 hr, pentamethylene congener **1b** (where the bicyclic tetraene valence isomeric form now predominates[10]) was converted to **4b** (mp 123–125° dec) in 87.5% yield. At higher temperatures (toluene, reflux), the hydrocarbon exhibited conversion directly to **3b** in 15% yield. This rearrangement was also monitored by deuterium labeling. When recourse was made to **1b**-*12,13-d$_2$*,[11] cyclooctatetraene **5b** was isolated with high positional specificity as determined from the nmr spectrum of **6b** in tandem with computer simulation.

Further studies with other group VI metal carbonyls have given evidence of a unique role for molybdenum. Thus, W(CO)$_6$ reacted at a convenient rate with **1a** only in hot xylene to give the thermoinactive tungsten analog of **4a**, mp 103–105°, in 45% yield after 14 hr. Complex formation with Cr(CO)$_6$ also proved sluggish, requiring 36 hr in refluxing toluene to achieve 28% conversion to the stable tetrahapto complex, mp 93–95°. In both instances, the recovered hydrocarbon gave no evidence of rearrangement.

If correlations with metal–carbon bond strengths[12] are involved, then these reactions would expectedly be favored by the weaker coordinating capability of molybdenum. Although a detailed mechanistic explanation of our observations must await a more generalized study, a first illustration is provided of the influential role capable of being exerted by metal carbonyl reagents on those orbital symmetry controlled processes in which π-bond interactions gain importance.

(7) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(8) L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1713 (1973).

(9) The calculated spectra of **6**-*1,2-d$_2$* and **6**-*1,5-d$_2$* differed greatly in the bridgehead and cyclobutane regions. The parameters employed in the computer simulation were derived from the unlabeled adduct and are as follows: $H_{2,5} = \delta\ 3.34$; $H_{1,6} = 4.02$; $H_{7,8} = 6.485$; $J_{7,8} = 8.0$; $J_{1,8} = J_{6,7} = 6.6$; $J_{2,5} = 6.0$; $J_{1,2} = J_{5,6} = 3.5$; $J_{1,7} = J_{6,8} = 1.2$; $J_{1,6} = J_{2,5} = J_{5,7} = 0.5$ Hz; and all other coupling constants equal zero.

(10) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **93**, 4516 (1971).

(11) The synthesis consisted of a direct modification of the method designed previously for the preparation of **1a**-*11,12-d$_2$*.[1] Details will appear in a later full paper on this subject.

(12) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969); R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

Commission for partial support and Ronald K. Russell for assistance with the computer simulation programs.

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Hierarchy of Orbital Symmetry Allowed Pathways in the Thermal Skeletal Rearrangements of a Structurally Unconstrained Cyclooctatetraene

Sir:

Thermal activation of 1,2-disubstituted cyclooctatetraenes (1) at temperatures above 400° in the gas phase causes *initial* skeletal rearrangement to the structurally isomeric 1,4 derivatives (2) in a process which is reversible.[1] The two most plausible hypothetical mechanisms for these intriguing reactions are (i) valence isomerization to a bicyclo[4.2.0]octatriene, followed by intramolecular Diels–Alder reaction and ultimate rearrangement of the resulting *cis*[2]-bishomobenzene intermediate, and (ii) a process again initiated by valence isomerization but now completed by [1,5] sigmatropic shift of an sp[2]-hybridized cyclobutene carbon and disrotatory opening of the relocated four-membered ring.[2] Pathway i has been shown to operate in unsaturated propellanes of type 3,[3] whereas sequence
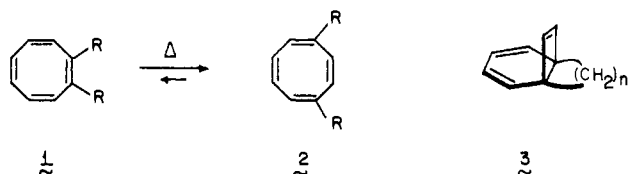
ii has been advanced as the mechanism which best explains the degenerate behavior of benzocyclooctatetraene-*3,8-d₂*.[1]

Such ancillary studies have not permitted a distinction between the two mechanistic avenues due to structural biases inherent in these systems which predispose them in opposite directions. Because knowledge of the hierarchic ordering of competitive symmetry-allowed processes such as i and ii commands special significance, we have sought to elucidate which of these thermal rearrangement pathways is most readily accessible to an *unconstrained* cyclooctatetraene derivative.

Experiments with 1,5-dimethylcyclooctatetraene (4)[4] make possible a resolution of this dichotomy. As a

(1) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 9224 (1972); M. Oku, unpublished results.

(2) A third possibility involving the intervention of bicyclo[3.3.0]-octadienediyls does not account satisfactorily for the observed translocation of substituents. Such intermediates do appear, however, to gain importance in other instances: M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964); M. Jones, Jr., and L. O. Schwab, *ibid.*, **90**, 6549 (1968); R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968); A. Roedig, G. Bonse, and R. Helm, *Chem. Ber.*, **106**, 2156 (1973).

(3) L. A. Paquette and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 4398 (1972).

(4) L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1713 (1973).

consequence of its symmetry, **4** can give rise in preliminary isomerization only to the two bicyclo[4.2.0]-octatrienes **5** and **6**. Although the values of the equilibrium constants for the **4** ⇌ **5** and **4** ⇌ **6** conversions remain as yet unknown, knowledge of these data is not necessary for the present purposes. This is due to the subtly parallel manner in which **5** and **6** can undergo further chemical change along either available reaction channel, a consequence of which is that the product mixture is independent of which triene is the reactant. As Scheme I shows, should either **5** or **6** transmute ac-

Scheme I
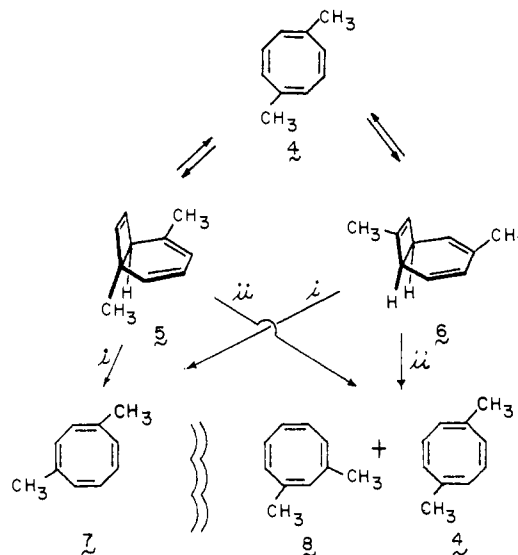
cording to mechanism i, convergence to 1,4-dimethyl-cyclooctatetraene (**7**) will result. In equally diagnostic fashion, operation of the [1,5] sigmatropic shift pathway (ii) will lead to 1,3-isomer **8** or return formally unchanged **4** depending upon which cyclobutene carbon acts as the pivot. It follows, therefore, that careful product analysis of the thermal rearrangement of **4** with increasing temperature should permit resolution of these unanswered questions. We now report such experiments which show $k_i > k_{ii}$.

Gas-phase pyrolysis of isomerically pure **4** (diluted with nitrogen) in a flow system at 415–435° and 18 mm for short contact times (1–3 sec) proceeded to 8–14% conversion and afforded exclusively **7** (Table I). Only

Table I. Product Composition Data from the Pyrolysis of **4**

Temp, °C	Pressure, mm	Recovery, %[a]	1,2-(9), %	1,3-(8), %	1,4-(7), %	1,5-(4), %
395	18	80				100
415	18	77			8	92
435	18	70			14	86
465	18	66	3	7	19	71
480	18	53	6	12	22	60
500	18	51	8	23	29	40

[a] Values relate to cyclooctatetraenes isolated upon vpc purification and do not include aromatic products.

when the temperature range was extended to 465° did minor amounts of **8**[5] and **9** make their appearance.

(5) This hydrocarbon was prepared in an isomerically pure state by thermolysis of 1,3-dimethylsemibullvalene (78% yield) in the same flow apparatus at 400° and 35 mm. Full details of this synthetic sequence will appear elsewhere.