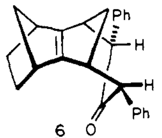

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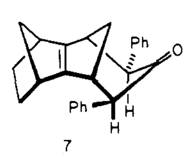

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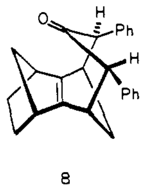

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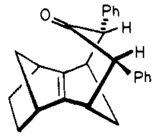

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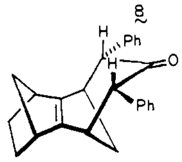

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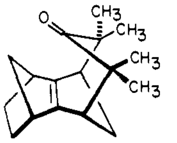
Comparable exposure of **1** to the tetramethyloxyallyl cation ($Fe_2(CO)_9$ generation) resulted in the isolation of **11** and **12** (ratio 4:1). The directionality of carbon–carbon bond formation in these symmetrical adducts (^{13}C NMR) was established by subjecting **11** to X-ray analysis.[13]



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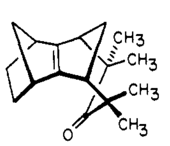
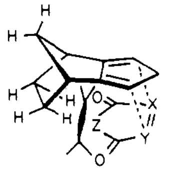


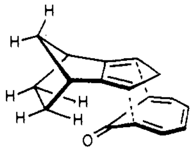
12

Thus, intermolecular [6 + 4] and [3 + 4] cycloadditions to **1** can be used to assemble norbornenyl-fused 4-cycloheptenones. The carbon frameworks of these end products reflect a face selectivity preference (above plane) that is opposite to that (below plane) observed for the majority of [4 + 2] processes involving this diene. Accordingly, the present observations are consonant with the Gleiter theory.

An alternative hypothesis is that above-plane stereoselectivity in **1** should always be preferred on steric grounds. Indeed, we now recognize that the ethano bridge structurally inhibits endo [4 + 2] addition as in D, whereas the methano bridge does not do so on all occasions. We have reasoned earlier[1] that highly reactive dienophiles (e.g., triazolinediones and maleic anhydride) prefer above-plane bonding to **1** because the associated early transition states place heavy emphasis on stabilizing secondary orbital effects and consequently are more demanding of the Alder (endo) capture. An overriding sensitivity to *long*-range steric factors therefore develops in these specific instances. However, [6 + 4] cycloadditions unambiguously adhere to exo-bonding schemes.[11,16] Accordingly, tropone has available to it only options E and F. Comparable transition states are less strongly favored in [3 + 2] cycloadditions.[17] A great deal less prima facie evidence for steric control in either transition state is apparent. In fact, the prevalence of **8** and **9** indicates that above-plane oxyallyl cation approach to **1** parallels that in F. From the relative proportions of **6** and **7**, the 180° alternative (i.e., C–O bond externally oriented) is preferred during below-plane cycloaddition.



D



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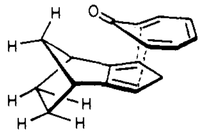

F

Since product equilibrations could not be effected, adduct formation seemingly occurs under kinetic control. The role of product stability on the observed stereoselection remains unclear, but is probably not significant. For example, ketones **6**–**12** differ insignificantly in their pyramidalized central double bond geometry.[13,18] Consequently, to the extent that long-range steric control can be discounted, orbital tilting within **1** must continue to be reckoned with as a force that contributes to π-face stereoselectivity.[19]

Supplementary Material Available: Tables listing crystallographic details for **5**, final positional and thermal parameters, bond distances, bond angles, $|F_o|$, and $|F_c|$ (23 pages). Ordering information is given on any current masthead page.

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[18] In an ancillary experiment, **2** was noted to decompose in C_6H_6 solution at 80 °C, while **3** proved stable to these conditions.

[19] The authors thank the National Cancer Institute (Grant CA-12115) for generous finanical support.

Interrelationship of π-Bond Tilting and the Stereochemical Disposition of Substituents at C-2 and C-7 within Norbornyl-Fused 4-Cycloheptenones[1]

Leo A. Paquette,* Leh-Yeh Hsu,[2a] Judith C. Gallucci,[2b]
James D. Korp,[2c] Ivan Bernal,*[2c]
Tina M. Kravetz, and Susan J. Hathaway

Evans Chemical Laboratories
The Ohio State University
Columbus, Ohio 43213
Department of Chemistry, University of Houston
Houston, Texas 77004

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The pyramidalization of alkenes is currently a subject of intense interest.[3] X-ray crystal analysis of several *syn*-sesquinorbornenes has provided evidence that this ring system experiences large deviations from planarity about its central double bond.[4] To a lesser extent, structurally simpler norbornenes likewise exhibit equilibrium nonplanar character.[5] In contrast, most,[4a,c,d] though not all,[6,7] *anti*-sesquinorbornenes possess an essentially flat π bond. Photoelectron spectra obtained on parent hydrocarbons **1** and **2** reveal their IP's to be significantly lower than expected.[8]

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[1] Electronic Control of Stereoselectivity. 24. For Part 23, see: Paquette, L. A.; Hathaway, S. J.; Kravetz, T. M.; Hsu, L.-Y. preceding paper in this issue.

[2] These authors are responsible for the X-ray crystal structure analyses reported herein: (a) compounds **6** and **8**, (b) compounds **7** and **9**, (c) compounds **4** and **5**.

[3] Watson, W. H., Ed. "Stereochemistry and Reactivity of Pi System"; Verlag Chemie International: Deerfield Beach, FL, 1983.

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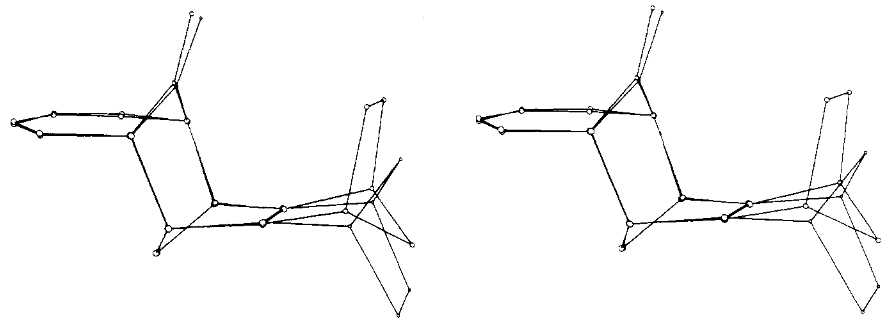
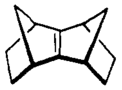


Figure 1. Stereoscopic overlap of **4** (larger circles) and **5** (smaller circles), which reveals the extensive central π-bond distortion in the first compound.

This experimental evidence has spawned substantial theoretical controversy.[9,10] While various effects have been underscored as responsible for the "rigid" π deformation in **1**, comparable



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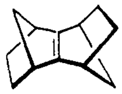

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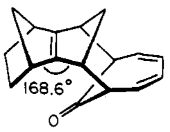
3

structural influences appear to be neutralized or absent in **2** and the unknown **3**.[10] However, a substantive weakening of their π-bond bending force constants has been calculated. It follows that hingelike deformation should be possible for **2** and **3**, though not for **1**. This communication describes X-ray studies on a group of six molecules possessing structural features similar to **1** and **2** but modified in order to acommodate a cyclohexanone ring molded into various conformations by a α,α′-substituents. In view of this new experimental evidence, the above criteria appear to have been too narrowly focused and may, in fact, be applicable to a wider range of molecules than heretofore appreciated.

The pair of tropone–isodicyclopentadiene adducts **4** and **5**[1] offer



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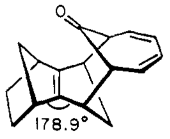

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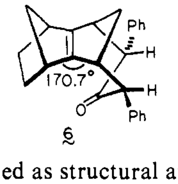
a complementary set of structural features. Both compounds share in common a butadiene bridge that is necessarily affixed diaxially to a typical cyclohexanone chair. Relevantly, however, the apical methylene groups in **4** are cis locked while those in **5** are projected to opposite surfaces. For **4**, the interplanar angle of 168.6° indicates a significant departure of the double bond from planarity. The statistically significant 11.4° deviation contrasts with that of **5** (1.1°) where the carbons about the central double bond constitute an essentially planar system. Stereoscopic comparison of ketones **4** and **5** is made in Figure 1.

In order to evaluate the possible importance of intermolecular contacts and extraneous ring strain effects, the three-dimensional structures of **6** and **7** were next determined. Both adducts[1] can



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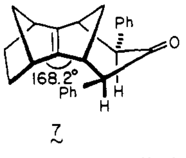
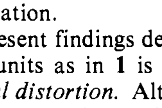


7

be regarded as structural analogues of **4**. A key distinction between **4** and **6** resides in the phenyl groups of the latter that are equatorially disposed. Nonetheless, the endocyclic double bond of **6** remains appreciably distorted from planarity (9.3°). Still more revealing is the large structural tilting in **7** (11.8°) that, in order to accommodate the substantial propensity of the phenyl rings to be equatorial, adopts boatlike cyclohexanone character. The similarity of the interplanar angles in **4**, **6**, and **7** eliminates the cyclohexanone conformation and axial/equatorial status of the α,α′-substituents as contributory to the phenomenon. All other intramolecular influences save the common *syn*-sesquinorbornene-related framework also appear to be discountable as causative factors.

In contrast, the molecular geometries of **8** and **9** relative to **5** point to the existence of an inherently weaker array of internal forces within the anti series. All three compounds are structurally



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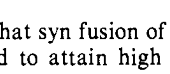

9

allied except for the translocation of the axial groups in **5** to equatorial environments within **8**. The tetrasubstituted nature of **9**[1] results in occupation of all four sites by methyl groups. Though **5** is not bent, both **8** and **9** are significantly distorted from planarity (11.2° and 9.8°, respectively). Variable equilibrium geometries within the central double bond of this subgroup are clearly apparent. Thus, the norbornene moiety in **5**, **8**, and **9** adjusts itself to an external dihedral angle that suitably accommodates the steric and electronic demands of more remote functionality centers. This variability is not evident in **4**, **6**, and **7**, presumably because the interplay of asymmetric forces does not follow comparable relaxation of an impressive level of pyramidalization.

The present findings demonstrate that syn fusion of two norbornene units as in **1** is not required to attain high levels of *pyramidal distortion*. Although defined molecular architecture is critical to the observation of this phenomenon, structural arrangements other than those found in *syn*-sesquinorbornene can deliver those influences contributory to inflexible π deformation. In our present view, the downward distortion in **4** relieves eclipsing and/or gives rise to the most favorable hyperconjugative interactions. Movement in either direction in **5** is counterbalanced; as matters improve on one surface, they worsen on the other. Finally, the 10–12° bending in **6**–**9** may indicate that the right-hand segments play the common role of closing down bond angles about the π linkage, thereby causing the norbornene unit to dictate entirely the resultant direction and extent of pyramidalization. Detailed calculations are currently in progress.

Acknowledgment. We gratefully acknowledge the financial support of the National Institutes of Health (Grant CA-12115 to LAP) and the Robert A. Welch Foundation (Grant E-594 to IB), as well as a helpful discussion with Professor K. N. Houk.

Supplementary Material Available: Data collection and processing parameters, atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles for all six ketones (85 pages). Ordering information is given on any current masthead page.

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