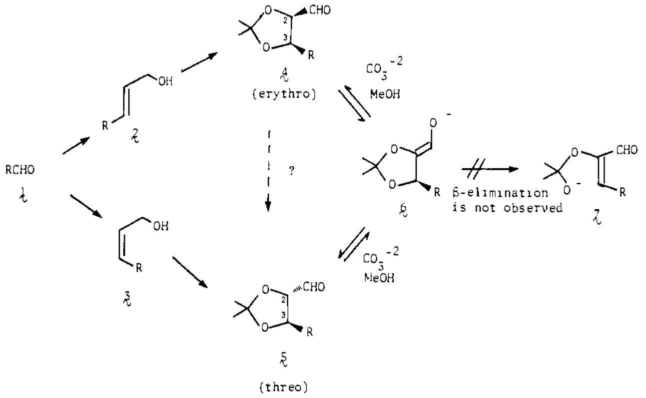
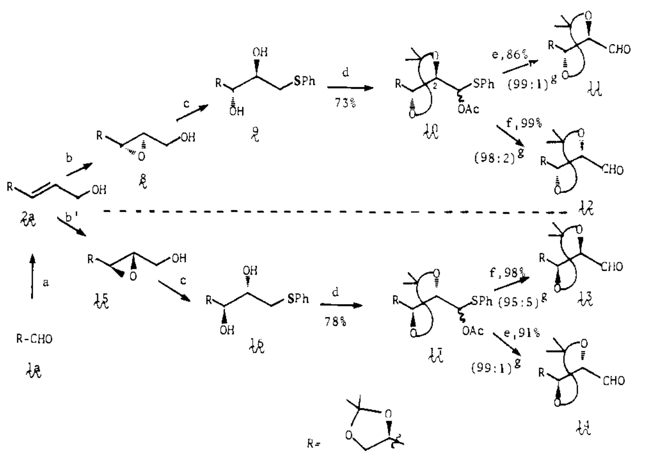
Scheme I

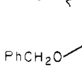
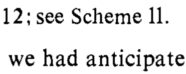


Scheme II.[a] Pentose Synthesis[b]



[a] This scheme shows a complete cycle of the iterative sequence for adding two new chiral centers in any one of the four possible ways. [b] Letters a-g refer to the following: (a) See ref 1, (i) $Ph_3P{=}CHCHO$ (toluene) 0 °C, 39 h, (ii) $NaBH_4$ (MeOH) −40 °C, 10 min; (b) $Ti(O\text{-}i\text{-}Pr)_4$, (−)-DET, TBHP ($CH_2Cl_2$) −20 °C, 15 h; (b′) $Ti(O\text{-}i\text{-}Pr)_4$, (+)-DET, TBHP ($CH_2Cl_2$) −20 °C, 15 h; (c) PhSH, 0.5 N NaOH, $(CH_3)_3COH$ (1:1) 100 °C, 3 h; (d) (i) $CH_3(CCH_2)OMe$, camphorsulfonic acid (CH_2Cl_2) 25 °C, 3 h, (ii) *m*-CPBA (CH_2Cl_2) −78 °C, 1 h, (iii) Ac_2O, NaOAc, reflux, 8 h; (e) see text; (f) see text; (g) see footnote 8.

Table 1. Base-Catalyzed Epimerization of *erythro*-4 to *threo*-5 Acetonides

erythro isomer	threo isomer	R in 4 and 5	5:4 (equilibrium)
4a	5a	$PhCH_2OCH_2$-	97:3
4b	5b		98:2[a]
4c	5c		>95:5

[a] The ratio observed for 12; see Scheme II.

an even better ratio than we had anticipated at the outset! The major product was shown to have the arabinose configuration in a manner similar to that employed for correlation of **11**. The acetonides (**13** and **14**) of the two remaining pentoses, xylose and lyxose, are prepared in exactly the same manner. The transformation of **2a** through **15** and **16** to **17** proceeds smoothly, and conversions of **17** into **13** and **14** are effected flawlessly. In this way a highly efficient route from the same intermediate to either the *erythro*- or the *threo*-2,3-dihydroxy aldehydes has been established.

A pleasing quality of the sequence shown in Scheme II is its symmetry. With an achiral R group, all structures and reaction steps (including reagents) above and below the dotted line have a perfect mirror image relationship. With a chiral R group, it will be recognized that the titanium-catalyzed epoxidation with a (+)- or (−)-tartrate overrides the influence of the preexisting chirality in the allylic alcohol by exhibiting high enantiofacial selection.[9] Now that efficient, practical routes from a chiral or achiral aldehyde to all of the four possible homologated aldehydes have been established, these four final products are ready for a second two-carbon extension, a central feature incorporated in our approach. Thus, the tetroses should lead to saccharides with an even carbon number and the pentoses to those with an odd number. Our efforts toward these larger saccharides including fragments of palytoxin have been successful even in the case of labile 2,3-erythro aldehydes such as **11** and **14**. These results will be documented in due course.

Acknowledgment. We are grateful to the National Science Foundation, Eli Lilly (unrestricted grant to K.B.S.) and Hoffmann-La Roche (unrestricted grant to S.M.) for generous financial support. V.S.M. thanks the Fundacion Juan March of Spain for a fellowship. High-resolution mass spectra were provided by the facility supported by the National Institutes of Health (Grant RR 00317, the Biotechnology Resources Branch, Division of Resarch Resources).

Registry No. 2a, 80532-35-0; **4a**, 81801-08-3; **4b**, 50866-82-5; **4c**, 81789-99-3; **5a**, 81801-09-4; **5b**, 13039-93-5; **5c**, 81769-40-6; **8**, 80532-36-1; **9**, 81769-41-7; **10**, isomer 1, 81769-42-8; 10, isomer 2, 81769-43-9; **11**, 50866-82-5; **12**, 13039-93-5; **13**, 13039-94-6; **14**, 81801-10-7; **15**, 80581-19-7; **16**, 81801-11-8; **17**, isomer 1, 81769-44-0; **17**, isomer 2, 81769-45-1.

Supplementary Material Available: Listing of spectra data and specific optical rotations for all new compounds prepared in this work (2 pages). Ordering information is given on any current masthead page.

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(9) Excellent stereochemical *control* in the construction of acyclic systems can often be achieved through the use of a enantioface-selective reagent, which outweighs the many other factors influencing the stereochemical course of a reaction. For a recent clear demonstration of this strategy, see: Masamune, S.; Ali, Sk. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557. For an applications, see: Masamune, S.; Hirama, M.; Mori, S.; Ali, Sk. A.; Garvey, D. S. *J. Am. Chem. Soc.* **1981**, *103*, 1568.

(10) **Note Added in Proof**: After the submission of this manuscript a report similar, in content, to our first communication[1a] appeared: Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109.

Planar *cis*-[10]Annulene and Azulene Revisited

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Aromatic character has proven to be a particularly enduring concept.[1] The central issue in the area of annulene chemistry revolves around the question of the ring size at which [4*n* + 2]annulenes become nonaromatic. This is generally taken to be the point at which the C–C bonds of the perimeter are no longer of equal length but alernate so as to produce a cyclopolyene with a succession of conjugated single and double bonds.[2-3] For some time now attention has been focused on [18]annulene in the belief that this molecule might well be close to the demarcation point between bond equalization and bond alternation in the annulenes.[2-4] Recently, however, theoretical work has suggested that

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(1) Garratt, P. J. "Aromaticity"; McGraw-Hill; London, 1971.

(2) Longuet-Higgins, H. C.; Salem, L. *Proc. Roy. Soc. Ser. A* **1959**, *251*, 172.

(3) Salem, L. "Molecular Orbital Theory of Conjugated Systems"; Benjamin: New York, 1966, Chapter 8.

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Table I. Calculated Structures and Energies for Planar *cis*-[10]Annulene (**1**)

	geometry		energy			
molecule	method	bond length, Å	method	total, hartrees	rel, kcal/mol	ref
1a	STO-3G	1.392	STO-3G	−379.61714	0.0	5b
1b	STO-3G	1.341, 1.457	STO-3G	−379.61120	−3.73	5b
1a	4-31G	1.386	4-31G	−383.78144	0.0	5b
1b	4-31G	1.373, 1.401	4-31G	−383.78148	−0.03	5b
1a	6-31G*	1.391	6-31G*	−384.32960	0.0	5c
1b	6-31G*	1.361, 1.426	6-31G*	−384.33041	−0.51	5c
1a	6-31G	1.392	6-31G	−384.19419	0.0	
1b	6-31G	1.376, 1.408	6-31G	−384.19420	−0.01	
1b	STO-3G	1.341, 1.457	6-31G	−384.18968	2.83	
1a	6-31G	1.392	MP2/6-31G	−385.08450	0.0	
1b	6-31G	1.376, 1.408	MP2/6-31G	−385.08265	1.16	
1b	STO-3G	1.341, 1.457	MP2/6-31G	−385.06904	9.70	
1a	MP2/6-31G	1.417	MP2/6-31G	−385.09306		

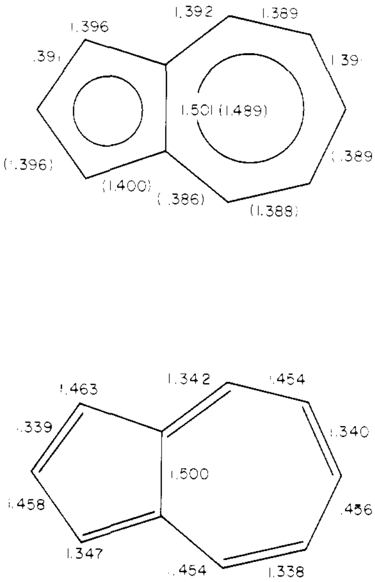

Figure 1. STO-3G (6-31G) calculated structures for azulene (**2**) in C_{2v} and C_s symmetry.

bond alternation might occur at much smaller ring sizes, namely in the planar *cis*-[10]annulene (**1**).[4k,5] It has been asserted[4g,4k] that electron correlation greatly favors the bond-equalized structure over the bond-alternate configuration of an annulene, and as a result these single determinant Hartree–Fock (HF) treatments could not be considered definitive. A virtually identical situation has arisen with respect to azulene (**2**), which has also been found to be bond alternate with single-determinant theoretical methods.[4k,5c,6]

In this communication we report the results of ab initio calculations on **1** and **2** that include the effects of electron correlation at the second-order Moller–Plesset (MP2) perturbation level.[7-9] The geometry of **2** (Figure 1) was fully optimized with the 6-31G[10] and STO-3G[11] basis sets within the HF approximation, while the structure of **1** was calculated at the HF/6-31G and MP2/6-31G levels.

It may be seen from Table I that for [10]annulene all of the HF treatments favor the bond-alternate structure **1b**, although the energy differences are small. At the highest HF level (6-31G*)[5c] **1b** is preferred by just over a half kcal/mol. The inclusion of electron correlation (MP2) in the optimization reverses this preference at the 6-31G level, and **1a** becomes the only minimum on the planar *cis*-[10]annulene potential surface. Furthermore, it can be seen that electron correlation becomes progressively less effective as the distortion increases. Hence electron-correlation effects are at a maximum in the bond-equalized geometry. This comes about because the higher symmetry of the bond-equalized geometry prevents the mixing of some configurations at the HF level which are included as the symmetry is reduced. The inclusion of electron correlation allows the treatment of the whole potential surface on an even footing. Furthermore as the HOMO–LUMO energy difference increases with the distortion of the molecular framework, the correlation-energy contribution decreases (perturbation theory). The correlation energy difference between **1a** and **1b** is small only because the extent of bond alternation in **1b** is very small at the 6-31G level. Analysis of the pair correlation energies shows that almost all the loss of correlation on distortion comes from the degenerate pair of highest occupied molecular orbitals (DPHOMOs). Thus for the MP2/6-31G calculations in Table I at the series of geometries **1a** (6-31G), **1b** (6-31G), and **1b** (STO-3G), in which the degree of bond alternation is progessively increased, the relative correlation energy for all the active electron pairs is 0, −1.17, and −6.87 kcal/mol, whereas from the DPHOMOs alone the relative correlation energy is 0, −0.93, and −6.64 kcal/mol.

Although the inclusion of polarization functions on carbon favors the bond-alternate structure,[5c] it appears that this effect will be insufficient to reverse our finding in favor of bond equalization in planar *cis*-[10]annulene. We believe that our results on **1** have implications for the field of annulene chemistry in general. It seems that [10]annulene may indeed be approaching the limit for bond equalization in the [4*n* + 2] annulenes (based on the flat potential surface found for **1**). However, there are a number of important provisos to this statement. It now seems clear that *the transition from bond equalization to bond alternation will be gradual and the degree of distortion will be small in borderline cases* (cf. Table I). As a result the experimental detection of symmetry breaking in such situations may be extraordinarily difficult, for the changes in associated physical

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(4) (a) Blattmann, H.-R.; Heilbronner, E.; Wagniere, G. *J. Am. Chem. Soc.* **1968**, *90*, 4786. Van-Catledge, F. A.; Allinger, N. L. *Ibid.* **1969**, *91*, 2582. (c) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613, 3635. (d) Oth, J. F. M.; Bunzli, J.-C.; de Zelicourt, Y. deJ. *Helv. Chim. Acta* **1974**, *57*, 2276. (e) Dewar, M. J. S.; Haddon, R. C.; Student, P. J. *J. Chem. Soc., Chem. Commun.* **1974**, 569. (f) Otsubo, T.; Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2449. (g) Baumann, H. *Ibid.* **1978**, *100*, 7196. (h) Vogler, H. *J. Mol. Struct.* **1979**, *51*, 289. (i) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722. (j) Haddon, R. C. *Chem. Phys. Lett.* **1980**, *70*, 210. (k) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431. (l) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1420. (m) Haddon, R. C. *Pure Appl Chem.* **1982**, *54*, 1129.

(5) (a) Loos, D.; Leska, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 187. (b) Farnell, L.; Kao, J.; Radom, L.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1981**, *103*, 2147. (c) Haddon, R. C.; Wasserman, Z. *Nouv. J. Chim.* **1981**, *5*, 357.

(6) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

(7) Mollar, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(8) Binkley, J. S. Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229.

(9) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE*, **1981**, *13*, 406.

(10) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(11) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

Table II. Calculated Energies for Azulene (2)

geometry method	method	energy: total, hartrees: 2a	energy: total, hartrees: 2b	rel (2a → 2b), kcal/mol	ref
MINDO/3	MB	−379.30297	−379.30775	−3.00	6
MINDO/3	STO-3G	−378.57956	−378.58932	−6.12	5c
MINDO/3	6-31G	−383.13311	−383.13546	−1.47	5c
MINDO/3	6-31G*	−383.26748	−383.27197	−2.82	5c
STO-3G	STO-3G	−378.59250	−378.59835	−3.67	
STO-3G	6-31G	−383.14649	−383.14229	2.64	
STO-3G	MP2/6-31G	−384.01822	−384.00616	7.57	
6-31G	6-31G	−383.14729			
6-31G	MP2/6-31G	−384.01645			

properties will be essentially imperceptible as the potential surface evolves from the flat single well encountered in **1** to a low-barrier double-minimum system. The structures will be averaged on a very short time scale, and analogy may be made with the difficulties encountered in the detection of (a)symmetrical hydrogen bonding.[12]

It is important to point out that while the propensity of the π-electron component toward distortion is roughly constant for a given value of N in an [$N = 4n + 2$]annulene, this is not always the case for the restoring force of the σ-bond component, which always favors bond equalization. This is best illustrated by the bridged annulenes,[4f,13-16] which clearly have a more rigid framework (supplied by the σ system) than their free-standing counterparts.[17-19] As a result the progression toward bond alternation may be quite different among annulenes with distinct σ-bond skeletal arrangements. In concluding this section we note that there are some [14]annulenes that may be exhibiting the slight degree of bond alternation mentioned above, although the small distortions were previously considered negligible and the structures thought to be effectively bond equalized.[20]

According to the HMO second-order Jahn–Teller theory of electronic structure, the tendency of azulene to adopt a bond-equalized geometry should be less than that of [10]azulene.[4i,21] Nevertheless, minimal basis set (MB) calculations[6] on the MINDO/3 structures for **2a** and **2b** favored the bond-alternate structure (**2b**), and in subsequent single-point HF calculations this preference was maintained (Table II). At the best theoretical level (6-31G*)[5c] the difference amounted to 2.8 kcal/mol. We have found that optimization of the structures with the STO-3G basis narrows the energy difference at the minimal basis set level while 6-31G calculations reverse the previous structural findings so that **1a** is the only minimum on the azulene potential surface at this theoretical level. Finally the inclusion of electron correlation effects (MP2) opens up a sizable energy gap in favor of **2a**.

As noted previously,[6] however, the HF calculations on azulene give large dipole moments of which the results obtained for **2b** are in best agreement with the experimental values of 0.80[22] and 1.08[23] D. The HF calculations give the following (in debye) 1.92 (**2a**), 1.40 (**2b**) [MB (wave function)//MINDO/3(geometry)];[6] 1.81 (**2a**), 1.17 (**2b**) [STO-3G]; 1.73 (**2a**) [6-31G]. We therefore assessed the efects of electron correlation by calculating the dipole moments using finite-field perturbation theory at the MP2/6-31G level. Such a coupled HF-based perturbation approach with a given basis has been shown to give molecular properties in very good agreement with large-scale configuration interaction calculations.[24,25] The results obtained [1.23 D (**2a**)] leave little doubt that azulene retains a bond-equalized perimeter (**2a**). The effect of electron correlation on the dipole moments is particularly dramatic in the present instance as the important HOMO → LUMO configurations effectively transfer charge density back from the five-membered ring to the seven-membered ring and thereby significantly reduce the total dipole moment, which is a maximum at the HF level for the symmetrical structure **2a**.

Registry No. **1**, 34067-24-8; **2**, 275-51-4.

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(12) (a) Brown, R. S.; Tse, A.; Nakashima, T.; Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 3157. (b) Svensson, C.; Abrahams, S. C.; Bernstein, J. L.; Haddon, R. C. *Ibid.* **1979**, *101*, 5759. (c) Haddon, R. C. *Ibid.* **1980**, *102*, 1807. (d) Jackman, L. M.; Trewella, J. C.; Haddon, R. C. *Ibid.* **1980**, *102*, 2519. (e) Rossetti, R.; Haddon, R. C.; Brus, L. E. *Ibid.* **1980**, *102*, 6913.

(13) Boekelheide, V. In "Proceedings of the Robert A. Welch Foundation", Milligan, W. O., Ed.; The Robert A. Welch Foundation, 1968; p 83. This book is "published by the Robert A. Welch Foundation" in USA W. O. Milligan, Editor.

(14) Vogel, E. In "Proceedings of the Robert A. Welch Foundation", Milligan, W. O., Ed.; The Robert A. Welch Foundation, 1968; p 215.

(15) (a) Masamune, S.; Brooks, B. W. *Tetrahedron Lett.* **1977**, 3239. (b) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 274. (c) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216.

(16) (a) Gilchrist, T. L.; Rees, C. W.; Tuddenham, D.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 691. (b) Gilchrist, T. L.; Tuddenham, D.; McCague, R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1981**, 657.

(17) Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.

(18) Van Tamelen, E. E. *Acc. Chem. Res.* **1972**, *5*, 186.

(19) Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, *5*, 272.

(20) (a) Vogel, E.; Deger, H. M.; Hebel, P.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 919. (b) Destro, R.; Pilati, T.; Simonetta, M. *Tetrahedron* **1980**, *36*, 3301. (c) Huber, W.; Lex, J.; Meul, T.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 391. (d) Vogel, E., private communication.

(21) Binsch, G.; Heilbronner, E.; Murrell, J. N. *Mol. Phys.* **1966**, *11*, 305.

(22) Tobler, H. J.; Bauder, A.; Gunthard, H. H. *J. Mol. Spec.* **1965**, *18*, 239.

(23) McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.

(24) Raghavachari, K.; Pople, J. A. *Int. J. Quant. Chem.* **1981**, *20*, 1067.

(25) Diercksen, G. H. F.; Sadlej, A. J. *J. Chem. Phys.* **1981**, *75*, 1253 and references therein.

Interconversions among the C_3H_4 Hydrocarbons: Photoisomerization of Allenes to Cyclopropenes and Methylacetylenes

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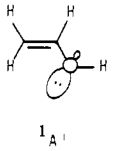
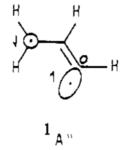
Received January 26, 1982

Considerable effort has been directed toward elucidating the electronic structure and geometry of vinylmethylene or vinylcarbene intermediates involved in thermal[1] and photochemical[2,3] ring-opening reactions of cyclopropenes. Detailed calculations[4] of potential-energy surfaces have provided insight for mechanistic understanding of cyclopropene ground-state[5] and singlet.[2,6] and triplet[7] excited state chemistry, and at least three species (I–III)



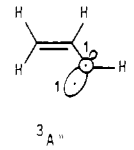
${}^1A'$

I



${}^1A''$

II



${}^3A''$

III

have been considered as intermediates. Such species have additional significance as potential intermediates in reactivity that

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(1) Greenberg, A.; Liebman, J. F. *Org. Chem.* **1978**, *38*, 91.

(2) (a) For a review see: Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310. (b) Padwa, A.; Blacklock, T. J.; Getman, D.; Naota, H.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481.

(3) There is evidence that vinylcarbenes are not necessarily intermediates in vinylcyclopropene rearrangements. (a) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493. (b) Zimmerman, H. E.; Hovey, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 2331.

(4) (a) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427. (b) Sevin, A.; Arnaud-Danon, L. *J. Org. Chem.* **1981**, *46*, 2346. (c) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482.

(5) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5681.

(6) Arnold, D. R.; Morchat, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 743.

(7) Pincock, J. A.; Moutsokapas, A. A. *Can. J. Chem.* **1977**, *55*, 979. (b) See ref 4 for theoretical treatments of cyclopropene triplet excited state potential surfaces. (c) For additional examples see ref 2.

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