Only the *Z* conformation of methyl thiolformate was found[2c] in the gas phase by microwave spectroscopy, and the similarity of the dipole moments in benzene (1.6 ± 0.1 D)[2c] and in the gas phase (1.58 ± 0.05 D)[2c] indicates that the *Z* conformation also predominates in the solution. We have found from a DNMR study of *tert*-butyl thiolformate in $CHClF_2/CHCl_2F$ (2:1) that the *Z* conformation also predominates in this compound (85% at −105 °C).[20] The phenyl group of phenyl thiolformate (**1**) cannot complete an aromatic sextet of the *Z* conformation, and it was expected that the *E* isomer of this compound would be appreciably populated in solution.

The NMR spectrum (90.02 MHz) of **1** in $CHClF_2/CHCl_2F$ (2:1) at +25 °C shows a single peak for the formyl proton at δ 10.16. At lower temperatures, the peak broadens and splits into two lines at δ 10.07 and 10.21, with populations of 0.60 and 0.40, respectively, at −104 °C.[21] A free-energy difference at this temperature of 0.13 kcal/mol was calculated from the relationship $\Delta G° = -RT \ln K$, and populations of 0.58 and 0.42 were estimated at the coalescence temperature (−80 °C), assuming that $\Delta G°$ does not change with temperature. Rate constants of 17 s^{-1} ($Z \rightarrow E$) and 23 s^{-1} ($E \rightarrow Z$) were obtained by comparison of the experimental spectrum at coalescence with theoretical line shapes[22] generated for different rate constants, and the corresponding free-energy barriers were calculated from the Eyring equation (10.1 ± 0.2 and 9.9 ± 0.2 kcal/mol at −80 °C).

Although steric interactions in planar **1** should destabilize the *Z* conformation, some evidence suggests that the phenyl group may actually be perpendicular to the rest of the molecule, and therefore the difference in steric interactions for the two conformations is probably small. The rotational barrier of thiophenol is only 0.8 kcal/mol, favoring the planar form,[23] while the resonance interaction for the lone pair and the phenyl group can be estimated[24] as $33|\sigma_R°| = 33(0.19)[24] = 6.3$ kcal/mol. Much of the difference between the resonance energy and the rotational barrier is probably due to stabilization of the transition state by interaction of an occupied orbital of the phenyl group with σ* of the SH bond.[25] Support for this interpretation comes from the effects of adding an electron to the benzene ring to form the radical anion[25] or adding an amino group in the para position;[26] in both cases, the perpendicular conformation is stabilized and becomes the preferred conformation. In phenyl thiolformate, the cross conjugation of the sulfur lone pair with the carbonyl group should make the sulfur a poorer π-donor to the benzene ring than in thiophenol and should also favor the perpendicular conformation. The *R* value for the CH_3COS group (+0.68)[27] is consistent with a nonplanar and possibly perpendicular orientation for phenyl thiolacetate and, by extension, for the thiolformate ester.

The available evidence then indicates that the phenyl group in **1** is not coplanar with the rest of the molecule[28] and that the small energy difference between conformations is due to the lack of aromaticity of the *Z* isomer, rather than to steric interactions. The percentage of the *E* isomer in *N*-phenylformamide is also high (27–55%),[5] compared to *N*-methylformamide (8%),[29] although the conformational equilibrium in this system will be affected by hydrogen bonding, and steric effects may also be important.

Registry No. **1**, 27064-03-5.

(19) Engler, v. R.; Gattow, G. *Z. Anorg. Allg. Chem.* **1972**, *388*, 78.

(20) A study of this compound in acetone-d_6 has been reported: Noe, E. A.; Sanders, T.; Badelle, F.; Douyon, L. *J. Am. Chem. Soc.* **1983**, *105*, 5918.

(21) The low-field/high-field peak area ratio increases in acetone-d_6 as solvent, indicating that the low-field peak is associated with the more polar *E* isomer.

(22) Calculated spectra were generated using a TRS-80 Model 4 microcomputer and a modified version of a program written by R. A. Newmark: Newmark, R. A. *J. Chem. Educ.* **1983**, *60*, 45. We thank Dr. Newmark for sending a copy of his program.

(23) Schaefer, T.; Wildman, T. A. *Chem. Phys. Lett.* **1981**, *80*, 280.

(24) Katritzky, A. R.; Topsom, R. D. *Chem. Rev.* **1977**, *77*, 639.

(25) Bernardi, F.; Mangini, A.; Guerra, M.; Pedulli, G. F. *J. Phys. Chem.* **1979**, *83*, 640.

(26) Schaefer, T.; Wildman, T. A.; Sebastian, R. *Can. J. Chem.* **1982**, *60*, 1924.

(27) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492. See also: Grunwell, J. R.; Hanhan, S. I. *Tetrahedron* **1973**, *29*, 1473 and references cited therein.

(28) Other evidence includes the relative barriers for **1** (9.9 and 10.1 kcal/mol) and for *tert*-butyl thiolformate in the same solvent (9.0 and 9.6 kcal/mol). The higher barriers for **1** suggest that the sulfur lone pair in this compound is not effectively cross conjugated with the phenyl group. The formyl proton of (*E*)-phenyl thiolformate absorbs at substantially higher field than for (*E*)-*tert*-butyl thiolformate (δ 10.21 vs. 10.73), while the corresponding difference is much smaller for the *Z* conformations (δ 10.07 vs. 9.97), with the *tert*-butyl compound absorbing at slightly higher field. A referee has noted that the upfield shift of the formyl proton of (*E*)-phenyl thiolformate is consistent with the proposed conformation; if the phenyl group in **1** is perpendicular to the plane of the formyl group, the formyl hydrogen should lie in the shielding region of the benzene ring. A comparison of the populations of the *E* isomers (0.40 and 0.15) and the barriers of **1** and *tert*-butyl thiolformate indicates that a steric effect is not a major factor in destabilizing the *Z* conformation of **1**. Phenyl thiolformate has both a higher population of the *E* conformation and higher rotational barriers. If the steric effect of the phenyl group were larger than for *tert*-butyl, the barriers for **1** would be expected to be *lower* than for *tert*-butyl thiolformate, as a consequence of destabilization of the planar ground states.

(29) LaPlanche, L. A.; Rogers, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 337.

General Approach for the Synthesis of Polyquinenes.[3] 2. Synthesis of Tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecane-2,5,8,11-tetraene

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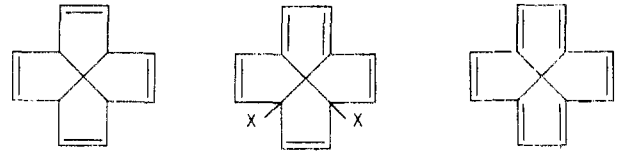
Tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecane-2,5,8,11-tetraene (**1**) has



1 **2**, X=H, or Br **3**

been a target of considerable interest to organic chemists for some time.[4-7] This stems, in part, from the desire to study the stability

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(3) For part 1 in this series, see: Venkatachalam, M.; Jawdosiuk, M.; Deshpande, M.; Cook, J. M. *Tetrahedron Lett.* **1985**, *26*, 2275 and references cited therein.

(4) The structure of **1** appears on the inside front cover of: Hendrickson, J.; Cram, D. J.; Hammond, G. "Organic Chemistry", 3rd ed.; McGraw Hill: New York, 1970. The tetraene **1** is contained in an assembly of compounds of theoretical interest of which only a few have been synthesized, including cubane (Eaton) and dodecahedrane (Paquette).

(5) (a) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. (b) Keese, R.; Pfenninger, A.; Roesle, A. *Helv. Chim. Acta* **1979**, 326. Schori, H.; Patil, B.; Keese, R. *Tetrahedron* **1981**, *37*, 4457. Mani, J.; Keese, F. *Tetrahedron*, in press. We thank Professor Keese for a preprint of this manuscript. (c) Hoeve, T.; Wynberg, H. *J. Org. Chem.* **1980**, *45*, 2930.

(6) Mitschka, R.; Oehldrich, J.; Takahashi, K.; Cook, J. M.; Weiss, U.; Silverton, J. V. *Tetrahedron* **1981**, *37*, 4521.

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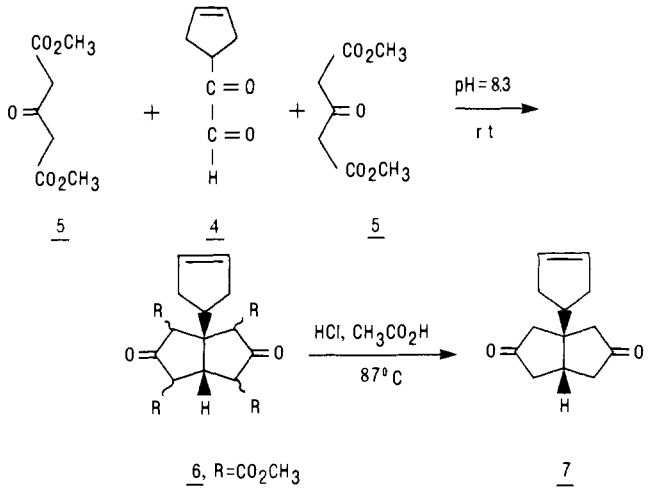
Scheme I

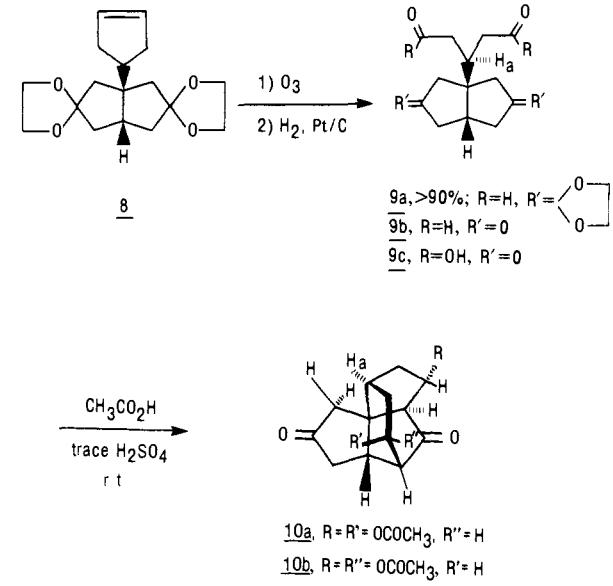


of highly strained polyquinenes[5,8] such as the fenestranes **2** and **3**[4-7] and also from the unique geometry (D_{2d} symmetry) of **1**.[4] The following report describes efforts which have culminated in an efficient synthesis of **1**.

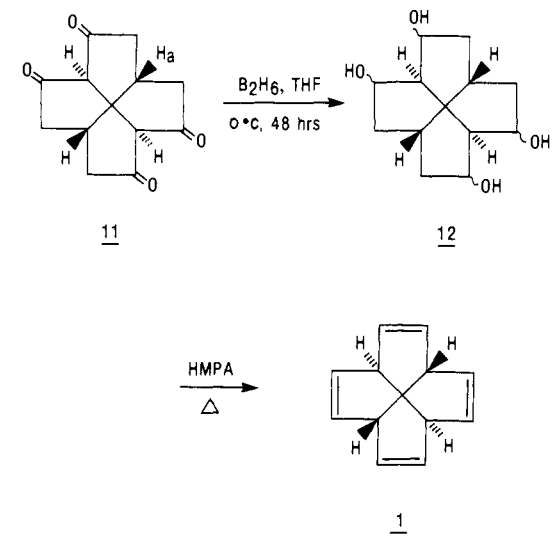
Earlier, the preparation of tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecane-2,6,8,12-tetraone (staurane tetraone) was reported.[9] Several attempts employing hydride reagents or pyridine borane[10] were made to convert the labile β-dicarbonyl groups of staurane-2,6,8,12-tetraone into functionalities more amenable for further transformations. These reductions gave complex mixtures of products which arose from cleavage reactions;[10] furthermore, it was shown that strained β-diketones readily undergo regiospecific cleavage of carbon–carbon bonds on treatment with nucleophiles.[11] For the above reasons the approach toward **1** was altered to avoid such labile β-diketones.

It was expected that conversion of **7** into a diketo dialdehyde followed by intramolecular aldolization would yield 2,6-dihydroxy staurane-8,12-dione thus avoiding the labile β-diketone functionality encountered earlier.[11] In fact, if intramolecular aldol cyclization were successful with the corresponding keto aldehydes, then the β-hydroxy ketones which would result could be trapped and retro-aldol cleavage reactions completely avoided. This approach has been successfully employed in our laboratory to prepare tetracyclo[6.6.0.$0^{1,5}$.$0^{8,12}$]tetradecane-3,6,10,13-tetraene.[3] The results of these experiments in the staurane series are outlined in Schemes I and II. Cyclopentene-3-glyoxal **4**[12] was stirred with 2 equiv of **5**, as shown in Scheme I, to provide a 90% yield of the *cis*-bicyclo[3.3.0]octane-3,7-dione system **6** as a crystalline solid. Hydrolysis of the β-keto ester functions accompanied by decarboxylation gave the pivotal intermediate **7**[13] in greater than 90% yield. The *cis*-bicyclo[3.3.0]octanedione,[7] after ketalization to provide **8**, was transformed (O_3; H_2, Pt/C) into **9a** in excellent yield. The dialdehyde **9a** was then stirred in acetic acid in the presence of a trace of sulfuric acid;[3] however, none of the desired [5.5.5.5]fenestrane derivative related to **1** was isolated. Instead,

Scheme II



Scheme III



the products of this sequence, obtained in 75% overall yield, were the two epimeric diketo diacetates **10a**[14] and **10b**.[15] The structures of **10a** and **10b** have been assigned on the basis of 2-dimensional correlated (COSY)[16] NMR as well as conventional (^1H, ^{13}C) NMR spectroscopy.[16] Evidently, during the formation (aldol) of **10a** and **10b**, the glutaraldehyde side chain (H_a = α) of **9a** (Scheme II) has cyclized with the stereochemistry indicated, while in the case of staurane tetraketone **11** the related diacid (glutaric) side chain has rotated 180° and the cyclization has occurred with the opposite stereochemistry at H_a (H_a = β, see **11**). The difference between the two modes of cyclization will be discussed, in detail, in a future report.[16] The parent diketo dialdehyde **9b** also gave the same two diacetates **10a** and **10b** when reacted under analogous conditions to those employed with **9a**.[17] Although the

(7) Lannoye, G.; Honkan, V.; Weiss, U.; Bertz, S.; Cook, J. M. "Abstracts of Papers", 10th Annual Meeting, Great Lakes American Chemical Society Region, Illinois State University, Normal, IL, June 7–9, 1982; No. 201.

(8) (a) Butenschön, H.; de Meijere, A. *Tetrahedron Lett.* **1984**, *25*, 1693. Butenschön, H.; de Meijere, A. *Tetrahedron Lett.* **1983**, *24*, 4563. (b) Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162.

(9) Mitschka, R.; Weiss, U.; Cook, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3973.

(10) Weringa, C.; Cook, J. M., unpublished results.

(11) Han, W. C.; Takahashi, K.; Cook, J. M.; Weiss, U.; Silverton, J. V. *J. Am. Chem. Soc.* **1982**, *104*, 318.

(12) This compound **4** can be made in three steps from commercially available cyclopentene-3-carboxylic acid. Bestmann, H. J.; Klein, O.; Gothlich, L.; Buckschewski, H. *Chem. Ber.* **1963**, *96*, 2259. Weygand, F.; Bestmann, H. J. *Chem. Ber.* **1957**, *90*, 1230.

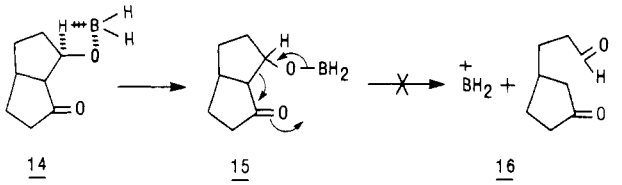
(13) **7**: mp 119–120 °C; ^{13}C NMR ($CDCl_3$) δ 35.2, 39.9, 44.0, 44.4, 47.1, 50.5, 129.9, 216.9.

(14) **10a**: mp 170 °C; IR (KBr) 1760, 1741 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 20.98 (q), 21.04 (q), 32.24 (t), 38.00 (d), 39.49 (d), 41.59 (t), 41.77 (t), 48.67 (t), 56.09 (d), 56.59 (s), 61.23 (d), 70.59 (d), 77.44 (d), 169.43 (s), 169.78 (s), 214.53 (s), 219.99 (s); high-resolution mass spectrum calcd for $C_{17}H_{20}O_6$ 320.1260, found 320.1295.

(15) **10b**: mp 159–160 °C; IR (KBr) 1751, 1737 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 21.04 (q), 21.07 (q), 32.14 (t), 41.87 (d), 41.97 (d), 42.78 (t), 48.15 (t), 53.61 (d), 56.39 (s), 61.39 (d), 72.32 (d), 77.30 (d), 170.15 (s), 170.28 (s), 214.73 (s), 214.94 (s); mass spectrum (CI, CH_4), *m/e* 321 (M + 1, 72%), 261 (83), 201 (100).

(16) Wehrli, S.; Deshpande, M.; Jawdosiuk, M.; Kubiak, G.; Lannoye, G.; Venkatachalam, M.; Weiss, U.; Silverton, J. V.; Cook, J. M., manuscript in preparation.

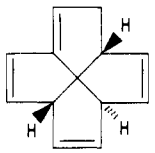
Scheme IV



14 15 16

products of transannular cyclization **10a** and **10b** are interesting in their own right, the failure of the "aldol approach" to provide the [5.5.5.5]fenestrane system was disappointing.

Because of the recent success in conversion of a related tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradecane-2,7,9,14-tetraone[16] into a tetrol via reduction by diborane–THF without ring cleavage, the analogous reduction of **11** seemed worthy of pursuit despite the negligible solubility of **11** in THF. Treatment of **7** (Scheme I) with osmium tetroxide, followed by oxidation with Jones reagent,[6] gave a 70% yield of the diketo diacid **9c** prepared earlier by Mitschka.[6,9] This diacid was cyclized to **11** under conditions previously reported.[6,9] The tetraketone **11** was then stirred in borane–THF[3] to provide a 92% yield of stereoisomeric tetrols represented by structure **12**[18] (Scheme III). The mixture of tetrols was then heated in refluxing HMPA[3,19] for 48 h to give staurane-2,5,8,11-tetraene (**1**)[20] (80%) accompanied by the bridgehead alkene **13**[21] (20%) in 61% overall yield. The tetraene **1** was



13

separated from **13** by flash chromatography. The solid that resulted was triturated with pentane and purified further by sublimation. Staurane-2,5,8,11-tetraene (**1**) is a white solid (mp 90 °C, sealed capillary) which will sublime on standing. The proton NMR spectrum of **1**, as expected, is very simple consisting of two singlets at δ 3.48 and 5.33. The IR spectrum of **1** is completely consistent with the assigned structure; moreover, the carbon NMR spectrum [δ ($CDCl_3$) 66.00 (s), 66.36 (d), 131.83 (d)] is definitive for a molecule with such D_{2d} symmetry.

The reason for the successful conversion of **11** into **12** without retro-aldol fragmentation can be readily discerned from the mechanism of diborane reduction, as illustrated in Scheme IV. Since the reduction is run in the absence of strong nucleophiles, the conversion of **14** into **15** can occur without carbon–carbon bond cleavage.[11] Rupture of the O–BH_2 bond (see **15**) to permit a retro-aldol reaction would generate the high-energy $^+BH_2$ species (see **16**) and hence does not take place. The diborane–THF reduction of **11** is significant for it has recently been employed for the reduction of other β-dicarbonyl systems related to **14**.[16] Since cleavage of the β-dicarbonyl carbon–carbon bonds of 2,8-dioxo-substituted *cis*-bicyclo[3.3.0]octanes (see **11** and **14**) can now be completely avoided, this method represents an important advance in the use of the condensation of 1,2-dicarbonyl compounds with **5** for the preparation of polyquinanes and polyquinenes.

The successful synthesis of **1** from **4** and **5** shows conclusively that the reaction of 1,2-dicarbonyl compounds with **5** serves not only as a route to natural products[22] and polyquinanes[4,23] but also provides a facile approach to polyquinenes. The 3,4-disposition of the two carbonyl groups (see **7** and **11**) in the diquinane framework is responsible for the simplicity of this approach. Research is in progress at present to study the chemistry of this tetraene **1**, as well as that of its bridgehead isomer **13**.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-7910302) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Frank Laib and Mary Rodgers for excellent technical assistance and Noel F. Wittaker for mass spectra.

(17) Deshpande, M.; Jawdosiuk, M.; Cook, J. M., unpublished results.

(18) One of the tetrols has been crystallized and characterized: mp 228–229 °C; ^{13}C NMR (CD_3OD) δ 42.33 (t), 49.38 (d), 69.75 (s), 69.91 (d), 78.31 (d); mass spectrum (CI/CH_4), *m/e* 241 (M + 1, 8), 223 (5.5), 205 (33.5), 187 (100), 169 (33). The remainder of the material, an oil, has been characterized by IR, NMR, and mass spectroscopy, as well as by high-resolution mass spectrometry.

(19) Monson, R. S. *Tetrahedron Lett.* **1971**, 567. Monson, R. S.; Priest, D. N. *J. Org. Chem.* **1971**, *36*, 3826. Lomas, J. S.; Sagatys, D. S.; Dubois, J.-E. *Tetrahedron Lett.* **1972**, 165.

(20) **1**: mp 90 °C (sealed capillary); IR (KBr) 3070, 2900, 1610 cm^{-1} (weak); ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 4 H) and 5.33 (s, 8 H); mass spectrum (EI), *m/e* 168 (M^+, 73), 167 (100), 166 (17), 165 (53); high-resolution mass spectrum calcd for $C_{13}H_{12}$ 168.0939; found 168.0958.

(21) **13**: This compound, an oil available in only small quantities, has been characterized by mass spectrometry and ^{13}C NMR spectroscopy. All other compounds gave satisfactory CH analysis and/or high-resolution mass spectra.

(22) Gymnomitrol: Coates, R. M.; Shah, S. K.; Mason, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 6765. Han, Y.-K.; Paquette, L. *J. Org. Chem.* **1979**, *44*, 3731. Isocomene: Dauben, W. G.; Walker, D. M. *J. Org. Chem.* **1981**, *46*, 1103. Modhephene: Wrobel, J.; Takahashi, K.; Honkan, V.; Lannoye, G.; Bertz, S. H.; Cook, J. M. *J. Org. Chem.* **1983**, *48*, 139. Pentalenene: Piers, E.; Karunaratne, V. *J. Chem. Soc. Chem. Commun.* **1984**, 959.

(23) Kubiak, G.; Weiss, U.; Cook, J. M. *J. Org. Chem.* **1984**, *49*, 561 and references cited therein.

syn-Sesquinorbornatriene and Its Quadricyclane Valence Isomer

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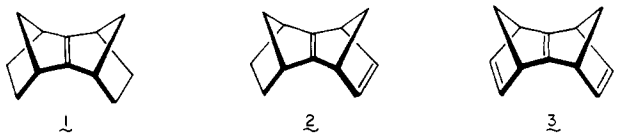
The small deviations from planarity experimentally observed about the double bond in structurally simple norbornenes[1] are recognized to be significantly amplified (to 16–18°) in derivatives of *syn*-sesquinorbornene (**1**).[2] The phenomenon has commanded



1 2 3

considerable theoretical attention.[3,4] More recently, introduction of a second double bond as in **2** has been found to enhance the level of downward pyramidal distortion (>20°)[5] and to be accompanied by substantial deshielding of the central olefinic carbon

(1) (a) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095. (b) Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *Ibid.* **1983**, *105*, 3642. (c) Mackenzie, K.; Miller, A. S.; Muir, K. W.; Manojlovic-Muir, Lj. *Tetrahedron Lett.* **1983**, 4747.

(2) (a) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105*, 3136. (c) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *Ibid.* **1983**, *105*, 3148. (d) Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. *Ibid.* **1984**, *106*, 5743.

(3) Norbornenes: (a) Wipff, G.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *74*, 400; *Tetrahedron Lett.* **1980**, 4446. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436. (c) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, 2435.

(4) *syn*-Sesquinorbornenes: (a) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, 927; *Tetrahedron* **1983**, *39*, 3345. (b) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (c) Jorgensen, F. S. *Tetrahedron Lett.* **1983**, 5289. (d) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135.

(5) (a) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232. (b) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.

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