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ALKYLIDENE DERIVATIVES OF *syn*-SESQUINORBORNATRIENE. ^{13}C NMR AND THEORETICAL ANALYSIS OF HOMOCONJUGATIVE ORBITAL INTERACTIONS

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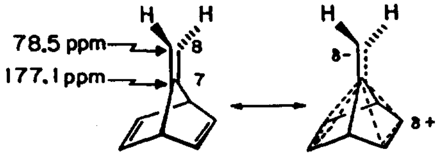
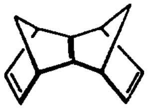
Summary: Despite downward folding of the central π linkage in 7 and 13, polarization of the exocyclic olefinic bonds does not surpass that seen in 1 and is not at all affected by cumulative carbomethoxy substitution of the peripheral unsaturated centers as in 9 and 10.

The unique electronic nature of methylenenorbornadiene (1)[1,2] is manifested in its large dipole moment (0.71D) and the widely divergent chemical shift of its exocyclic carbon atoms ($\Delta\delta = 98.6$ ppm). The pronounced homoconjugated character of its ground state (see 1b) is further substantiated by photoelectron (PE) spectroscopy,[1,3] which reveals the HOMO to be raised by 0.3 eV relative to norbornadiene because of crossed longicyclic interaction.[4] Since the extent of homoconjugation is closely linked to the size of the coefficient at C-7, the number and nature of substituents bonded to C-8 have pronounced spectroscopic consequences.[3,5,6]



1a   1b

2



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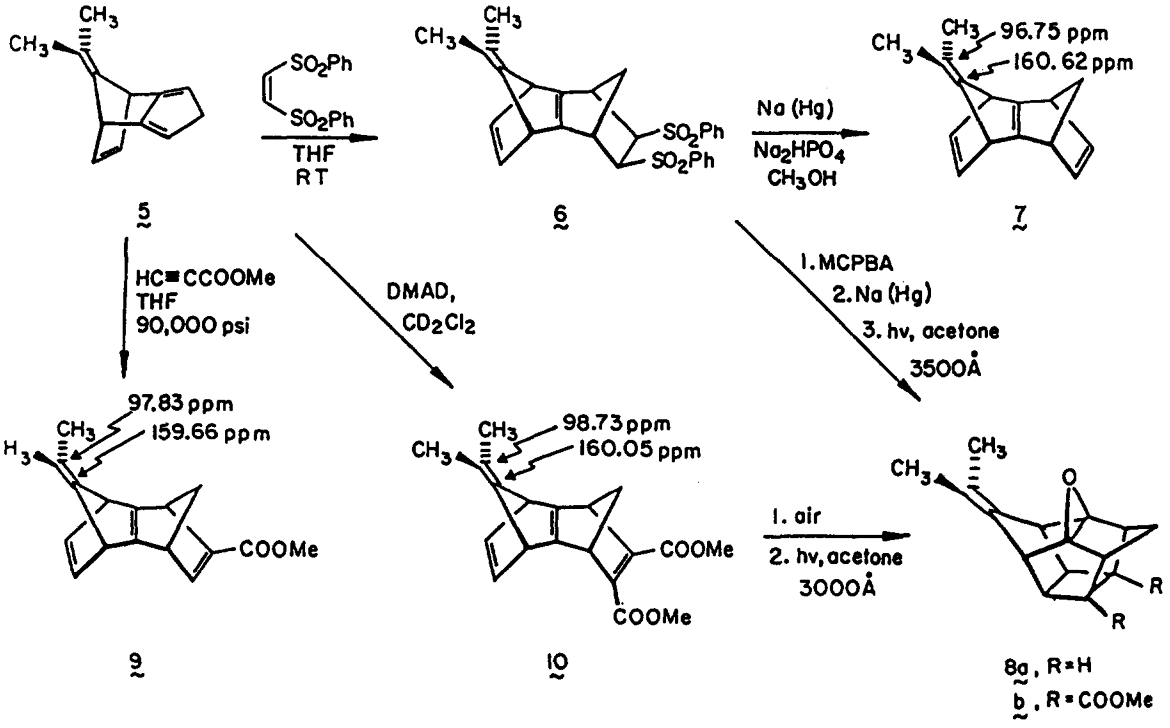
With the recent successful acquisition of *syn*-sesquinorbornadiene (2) and -triene (3),[7] we have been made well aware of the substantial downward pyramidalization of their central bonds. The relatively inflexible 15-20° deviation from planarity is recognized to heighten sensitivity to triplet oxygen and reactivity toward other reagents. However, the impact of increased above-plane pπ electron density on potential homoconjugation in suitable mono- and dialkylidene derivatives remained to be assessed. Our present results provide new insights into the requirements for effective homoconjugative interactions of this type.

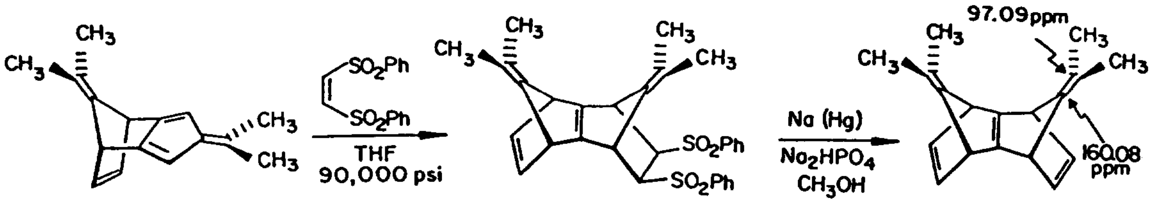
The synthesis of 7 was achieved by stirring 5 with (*Z*)-1,2-bis(phenylsulfonyl)ethylene[8] in THF at room temperature for 4 days, followed by reductive desulfonylation[9] of adduct 6 (Scheme I). Characterization of these products as syn stereoisomers was realized by sequential peracid oxidation, desulfonylation, and photocyclization of 6 to give 8a.[10] Likewise, dimethyl acetylenedicarboxylate (DMAD) added to 5 in CD_2Cl_2 at 20 °C during 24 h to deliver the air-sensitive diester 10. That below-plane Diels-Alder addition had again materialized was proven by [2+2] photo-induced closure of the epoxide to 8b. A practical rate of condensation of methyl propiolate to 5 in THF required 90,000 psi for 5 days at room temperature.

Scheme I



The "superfulvene" 11 likewise was dependent on high pressure conditions for reaction with the (*Z*)-disulfone (79%, Scheme II). Buffered 2% sodium amalgam acted on 12 to provide the highly reactive pentaene 13.

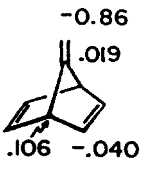
Scheme II



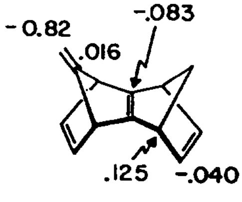
11 12 13

Unambiguous assignment of ^{13}C chemical shifts to all four *syn*-sesquinorbornatrienes was accomplished by making recourse to 2-D C/H correlation and COLOC experiments.[11] The recorded $\Delta\delta$ values of their exocyclic olefinic carbons (see formulae) are: 7 (63.9 ppm), 9 (61.8 ppm), 10 (61.3 ppm), and 13 (63.0 ppm). For comparison, the $\Delta\delta$ of 7-isopropylidenenorbornadiene is 72.0 ppm.[3,5] The internal consistency of $\Delta\delta$ in 7, 9, 10, and 13 is particularly striking. Neither the heightened symmetrization in 13 nor the electron-withdrawing effects of the carbomethoxy groups is felt at all!

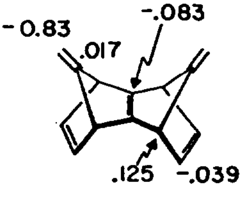
These experimental findings can be understood if proper consideration is given to the manner in which the π systems interact within the *syn*-sesquinorbornatriene framework. Since the chemical shift is a function of the electronic environment of the nuclei, the net charges within 1, 14, and 15 were calculated by the MINDO/3 method.[12] The charge polarization in the exo-methylene groups is seen to be somewhat more intense in 1 than in the other two.[13] This effect can be traced back to a stronger charge transfer from the three endo π-MO's of 14 and 15 back into the π*-MO's of their exo-methylene group(s).



1



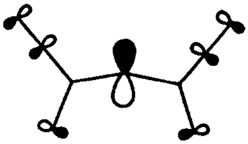
14



15

While the π*-MO's localized at the exocyclic double bonds of 1, 14, and 15 are predicted to reside at nearly the same energy (+1.8 to +2.1 eV), a significant change occurs in the endo π-MO's of 1 [$5b_1(\pi)$ = -9.10 eV] when compared to those in 14 and 15 [$12a_1(\pi)$ = -8.29 eV, $10b_2(\pi)$ = -8.89 eV]. This energy difference is in line with PE data on related species such as norbornadiene ($I_{v,1}$ = 8.69 eV)[14] and *syn*-sesquinorbornatriene ($I_{v,1}$ = 7.84 eV),[15] respectively. The smaller energy difference between the HOMO and π*-MO's of the exo-methylene groups in 14 and 15 is consistent with a stronger charge transfer as discussed above.

The negligible effect of the electron-withdrawing substituents in 9 and 10 can be rationalized by an examination of the HOMO of 15 (Figure 1). Since electron density is localized predominantly at the central double bond, peripheral substitution finds it possible only to weakly influence charge transfer from the HOMO to the π*-MO of the exo-methylene double bond.[16]



$12a_1(\pi)$

Figure 1

References and Notes

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(11) We thank Dr. Charles Cottrell of the Ohio State Campus Chemical Instrumentation Center for this measurement.
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