Synthesis and Spectroscopy of Tricyclo[3.3.3.0^{3,7}]undec-3(7)-ene: Confirmation of Computational Predictions Regarding the Effects of Pyramidalization on Alkene Ionization Energies and Electron Affinities

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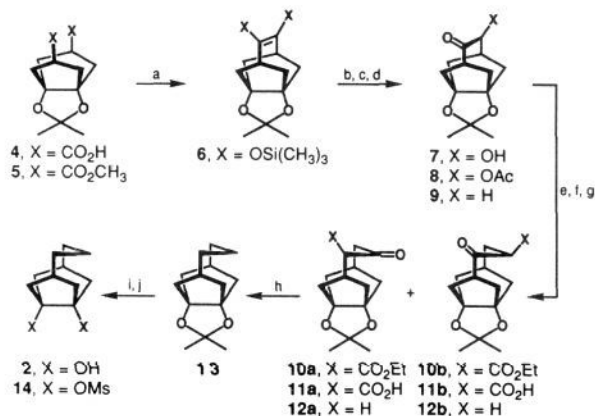*CH-1700 Fribourg, Switzerland*

We have reported the syntheses of the $n = 1$[1] and 2[2] members of a homologous series of pyramidalized alkenes (**1**),[3] their spectroscopic study in matrix isolation,[4,5] and some of their chemistry.[6] The generation of a benzo derivative of **1**, $n = 2$,[7] and a bis-ethano derivative of the $n = 0$ member of this series have also been described.[8] In this communication we report the synthesis and some spectroscopy of **1**, $n = 3$.

1   **2**   **3**
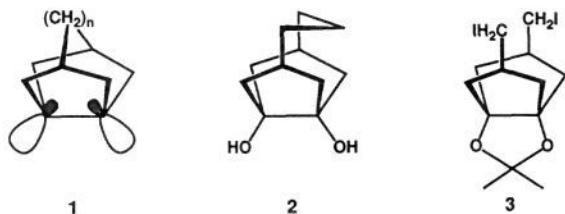
Previous attempts to prepare diol **2**, a promising precursor of **1**, $n = 3$, have been unsuccessful. Double ring expansion of bicyclo-[3.2.2]nonane-6,8-dione,[9] followed by transannular reductive ring closure,[10] failed when the ring expansion proceeded with the undesired regiochemistry.[11] Efforts to prepare **2** from diiodide **3** by a ring closure, analogous to the one that proved successful in the synthesis of the 10-selena derivative of **1**, $n = 3$,[12] foundered when both dithiane and malonate ester monoadducts of **3** failed to undergo cyclization under a wide variety of conditions.[13]

A third route to **2**, which incorporates features of the two unsuccessful pathways, has resulted in its synthesis.[14] As shown in Scheme I, we have formally inserted a methylene group between

Scheme I[a]

4, X = CO₂H
5, X = CO₂CH₃

6, X = OSi(CH₃)₃

7, X = OH
8, X = OAc
9, X = H

2, X = OH
14, X = OMs

13

10a, X = CO₂Et   **10b**, X = CO₂Et
11a, X = CO₂H   **11b**, X = CO₂H
12a, X = H   **12b**, X = H

[a] (a) Na, TMSCl, toluene, reflux, 67%; (b) CH₃OH, reflux, 84%; (c) acetyl chloride, DMAP, CH₂Cl₂, 82%; (d) SmI₂,[14] THF, 91%; (e) N₂CHCO₂Et, Et₃OBF₄,[15] CH₂Cl₂, 45%; (f) 5% NaOH, 98%; (g) p-dioxane, reflux, 82%; (h) N₂H₄, NaOH, diethylene glycol, 185 °C, 78%; (i) 20% AcOH, 85 °C, 81%; (j) CH₃Li, THF, then MsCl, 55%.

the two carboxylic carbons of diacid **4**[12] by performing an acyloin ring closure on dimethyl ester **5**, reductively removing[15] the hydroxyl group from **7**, and then ring expanding[16] ketone **9**. As in Leonard's synthesis of tricyclo[3.3.3]undecane (manxane),[17] the regiochemistry of the ring expansion step is irrelevant, since **12a** and **12b** both undergo Wolf–Kishner reduction to **13**. Hydrolysis of **13** affords diol **2** in 9.6% overall yield from **4**.

Diol **2** was converted to dimesylate **14**, which was reduced to **1**, $n = 3$, using either sodium naphthalide[12,18] or, more conveniently, sodium amalgam in ether. The latter method allows ether solutions of pure olefin to be obtained simply by filtering the reaction mixture. Unlike its lower homologues,[1-8] **1**, $n = 3$, is stable to dimerization at room temperature; but it reacts very rapidly with atmospheric oxygen.[19]

Careful exclusion of air from samples of the olefin allowed it to be characterized spectroscopically. A very weak band was observed in the IR at 1615 cm⁻¹, which corresponds to the strongest band in the Raman spectrum and is assigned to the C≡C stretch in the olefin. An RHF/3-21G[20] vibrational analysis[21] gives a frequency of 1851 cm⁻¹ for this mode. After scaling by 0.873,[22] in order to account for the effects of anharmonicity and electron correlation,[24] the C≡C stretching frequency in **1**, $n = 3$, is predicted to occur at 1615 cm⁻¹.

The C≡C stretching frequency found in **1**, $n = 3$, is 10 cm⁻¹ lower than that in its 10-selena analog.[12] The lower C≡C stretching frequency in and greater reactivity toward O₂ of the

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hydrocarbon is consistent with the fact that the doubly bonded carbon atoms in it are calculated to have larger pyramidalization angles ($\phi = 25.0°$ and $25.2°$)[25] than those found in a salt of the selenium analog.[12]

Both the ^{1}H and ^{13}C NMR spectra of **1**, $n = 3$, are temperature dependent. The identity of the protons and carbons whose resonances broaden and coalesce indicates that the dynamic process responsible for these spectral changes is flipping of the trimethylene bridge. From the frequency separations at low temperatures and the temperatures, T_c, at which coalescence was observed in the resonances for the *exo* and *endo* allylic protons and the allylic and olefinic carbons, values of $\Delta G^\ddagger = 14.6 - 15.0 \pm 0.2$ kcal/mol for bridge flipping were obtained at $T_c = 304–328 \pm 3$ K.[26] In very good agreement with these NMR results, MM2 calculations[27] predict that trimethylene bridge flipping should require 14.4 kcal/mol.

The average chemical shift of δ 157.28 for the olefinic carbons in **1**, $n = 3$, is larger than that of δ 150.74 in the 10-selena derivative[12] and that of δ 146.0[28] in bicyclo[3.3.0]oct-1(5)-ene (BCO),[29] the unbridged reference olefin. The monotonic change in these ^{13}C chemical shifts with increasing pyramidalization indicates that pyramidalization shifts the resonances for olefinic carbons to lower fields.[30]

Olefin **1**, $n = 3$, exhibits a UV absorption with $\lambda_{max} = 217 \pm 5$ nm in pentane. The more highly pyramidalized olefin, **1**, $n = 2$, has a UV absorption at even longer wavelength, $\lambda_{max} = 245 \pm 15$ nm.[5] In contrast, BCO does not show a UV maximum above 200 nm in solution. We find the maximum for the $\pi \rightarrow \pi^*$ singlet excitation in the electron energy loss (EEL) spectrum of BCO to be at 6.54 eV, which is close to the 6.61 eV reported for tetramethylethylene (TME)[31] and corresponds to a wavelength of 190 nm.

The experimental finding of a red shift in λ_{max} with increasing olefin pyramidalization is consistent with the results of *ab initio* calculations.[25,32] However, the calculations also predict that lowering the energy of the LUMO, rather than raising that of the HOMO, plays the dominant role in decreasing the HOMO–LUMO energy separation.[33] For example, RHF/3-21G calculations on **1**, $n = 3$, find that the HOMO energy is 0.25 eV higher than that of BCO; whereas the LUMO energy of **1**, $n = 3$, is computed to be 0.79 eV lower than that of BCO.[25] The predicted changes in the HOMO and LUMO energies appear to be rather insensitive to the basis set used.[34]

HOMO and LUMO energies can be related, respectively, to ionization energies (IEs) and electron affinities (EAs) via Koopmans' theorem.[35] We have used photoelectron (PE)[36] spectroscopy to measure the IEs of **1**, $n = 3$, and BCO and employed electron transmission (ET)[37] spectroscopy to measure their EAs. These spectra[14] confirm the prediction that the effect of pyramidalization on lowering the energy of the LUMO is much greater than its effect on raising the energy of the HOMO.[38]

The PE spectrum of BCO gives an adiabatic IE of 8.11 eV, which is close to that of 8.27 eV reported for TME.[41] The adiabatic IE of **1**, $n = 3$, is 7.80 eV, which is lower than that of BCO by 0.31 eV. This difference between the measured IEs is in very good agreement with the difference between the calculated HOMO energies.[25,34,42]

The ET spectrum of BCO gives a vertical EA of –2.44 eV, which again is close to the EA of –2.27 reported for TME.[43] However, the ET spectrum of **1**, $n = 3$, gives an EA of –1.70 eV. The 0.74 eV greater electron affinity of **1**, $n = 3$, is also in very good agreement with the difference between the calculated LUMO energies.[25,34]

This good agreement suggests that the calculations might also be able to predict which members of this series of pyramidalized olefins will form bound radical anions in the gas phase.[44] After scaling the computed difference of 3.50 eV between the LUMO energies of BCO and **1**, $n = 0$,[25] by the difference of 0.74 eV between the experimental EAs of BCO and **1**, $n = 3$, divided by the difference of 0.79 eV between their calculated LUMO energies,[25] our experimental value of EA = –2.44 eV for BCO indicates that **1**, $n = 0$, should have a vertical EA that is positive by 0.84 eV (0.26 eV if RHF/6-31G*//TCSCF/6-31G* LUMO energies[34] are used). Therefore, this most highly pyramidalized ($\phi = 61.2°$)[25] member of the homologous series of alkenes **1** is predicted to form a bound radical anion.[46] The chemistry observed for a bis-ethano derivative of **1**, $n = 0$,[8] is consistent with the prediction of a LUMO of very low energy in this alkene.

Supplementary Material Available: Synthetic details as well as spectroscopic and analytical data for **1**, $n = 3$, **2**, and **5–14** and figures containing photoelectron spectra and electron transmission spectra of **1** and BCO (21 pages). Ordering information is given on any current masthead page.

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