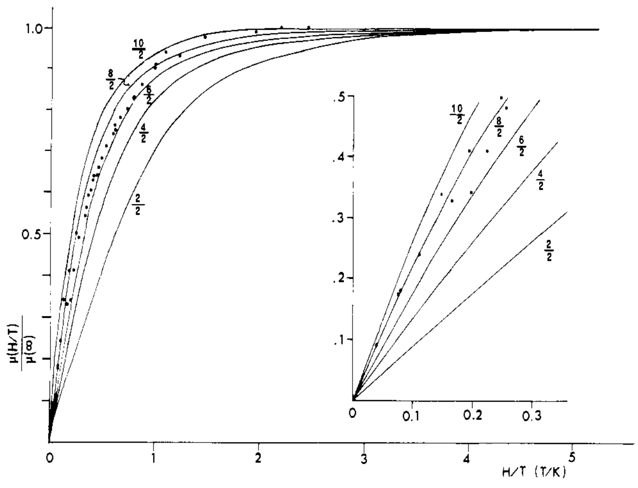

Figure 2. Plots of magnetization of **1** in 2-methyltetrahydrofuran vs. temperature-normalized field strength (H/T). Theoretical magnetization curves are given by the Brillouin function in which $J = S = {}^{2}/_{2}, {}^{4}/_{2}, {}^{6}/_{2}, {}^{8}/_{2}$, and ${}^{10}/_{2}$, the saturated values being normalized to 1.0.

ably because of the orientational fluctuation under these conditions. The slope of line A was found to give $\mu_{\text{eff}} = 9.33\ \mu_B$ and $n = 8.4$. The line has the first break point at 65 K and the line in region B has a negative Weiss temperature of −22 K, indicating that the paramagnetic species now feels the antiferromagnetic molecular field at temperatures lower than 65 K. After the second break point, the inverse of the paramagnetic susceptibility aims at the origin when plotted against temperature (region C). The observed behavior of the plots is highly reminiscent of the antiferromagnetic interaction in the trinuclear cluster of paramagnetic species.[4] Similar results were obtained when the initial concentration of **2** was raised to 3.56×10^{-2} M or microcrystals of neat **2** were photolyzed. The results show that **2** was dispersed in 2-MTHF as an aggregate when frozen at higher concentrations, generating **1** close enough to induce antiferromagnetic interaction between the molecules of **1**.[5]

Magnetization of **1** in 2-MTHF was measured as a function of the main field at several temperatures (2.1, 4.2, 9.0, 17.5, and 31 K). The striking feature is a large saturation effect on the magnetization of **1** at lower temperatures. Especially a complete saturation was observed in the magnetic field higher than 2.5 T at 2.1 K. The characteristic behavior of the saturation should be due to the high spin multiplicity of **1**. The experimental values plotted against the temperature-normalized field strength (H/T) were found to fit with a single curve (Figure 2). The correlation is rationalized in terms of the Brillouin function for magnetization:

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

where $x = gJ\mu_B H/(k_B T)$. The theoretical magnetization curves are given in Figure 2 for five high-spin states $J = {}^{2}/_{2}, {}^{4}/_{2}, {}^{6}/_{2}, {}^{8}/_{2}$, and ${}^{10}/_{2}$, the saturated values of each state being normalized to 1.0. Note that the curves are independent of the concentration of the electron spins. The experimental data are found to fit the theoretical curve with $J = {}^{8}/_{2}$ especially in the small H/T region where intermolecular magnetic interaction is not significant. Since the orbital angular momentum may be neglected for hydrocarbon **1** and therefore $J=S$, the above correlation provides another evidence for the nonet ground state of **1**. We propose this analysis as a simple and versatile method for determining the high spin multiplicity of paramagnetic samples of unknown concentration.

Lastly, the saturation behavior of magnetization of **1** is somewhat similar to that of ferromagnetic materials. The result suggests that the nonet polycarbene can be regarded as a "micro" domain in ferromagnets and that, as the spin multiplicity of polycarbenes becomes higher, the magnetization behavior will resemble closer that of ferromagnets.[6]

Registry No. 1, 85566-03-6; **2**, 85566-04-7.

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[6] The Fe fine particles with a size of 30 Å show superparamagnetic behavior. Magnetization of these particles (μ_{eff} = ca. 160 μ_B) obeys the Brillouin function just like a paramagnetic species, but the $1/\chi_p$ vs. T plot reveals the transition to a ferromagnet at 30 K (Yatsuya, S.; Hayashi, T.; Akoh, H.; Nakamura, E.; Tasaki, A. *Jpn. J. Appl. Phys.* **1978**, *17*, 335). Nonet carbene **1** may be regarded as an organic counterpart of the above superparamagnet and to constitute the "micro" domain of the ferromagnets.

Synthesis of *in,out*-Bicyclo[4.4.4]tetradecane. Generation of a Stable μ-Hydrido-Bridged Carbocation

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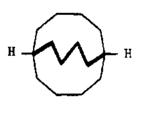
Received June 25, 1984

Although small-ring bicycloalkanes such as bicyclo[2.2.1]heptane (norbornane) and bicyclo[2.2.2]octane are well-known and much-studied, medium-ring bicycloalkanes, in which all rings are eight-, nine-, or ten-membered, are practically unknown. Only bicyclo[3.3.3]undecane (manxane) has been reported.[1,2] As pointed out by Alder,[3] however, this situation is unfortunate in view of the chemistry that might be expected for other medium-ring bicycloalkanes. For example, it has been predicted[4] that *out,out*-bicyclo[4.4.4]tetradecane (**1**) should have 60.5 kcal/mol strain energy as a consequence of severe transannular interactions and that its bridgehead chloro derivative should be some 10^7–10^9 more reactive toward solvolysis than *tert*-butyl chloride.



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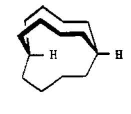

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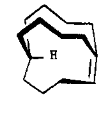

3

Perhaps more interesting, however, is that bicyclo[4.4.4]tetradecane should be capable of existence in more than one isomeric form. Because of the size of the four-carbon bridges, in,out isomer **2** with an inverted bridgehead carbon should also be possible and may,[3] in fact, be less strained than out,out isomer **1**. We have now synthesized in,out isomer **2** and bridgehead olefin **3** by the route indicated in Scheme I.

The route, starting from the known[5] keto alcohol **4**, is self-explanatory, with the key titanium-induced cyclization[6] of keto

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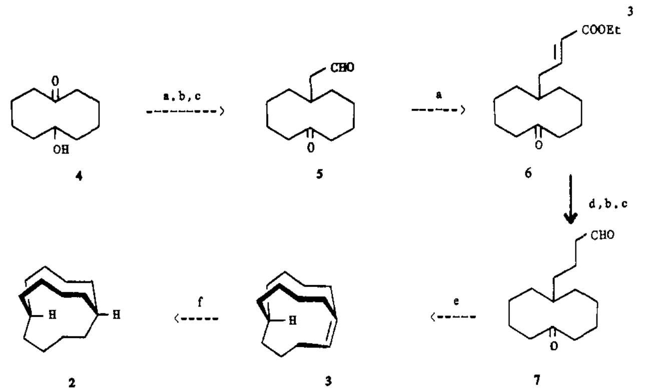
Scheme I^a

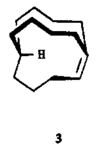


^{a} (a) (EtO)$_2$P(O)CH$_2$COOEt, NaH, THF; (b) LiAlH$_4$, THF; (c) pyridinium chlorochromate, CH$_2$Cl$_2$, NaOAc; (d) H$_2$, Pd/C, ethanol; (e) TiCl$_3$, Zn-Cu, dimethoxyethane, Δ; (f) H$_2$, PtO$_2$, ether, 50 psi, 3 days.

aldehyde **7** taking place in 30% yield to give *in*-bicyclo[4.4.4]-1-tetradecene (**3**).[7] In addition to in-isomer **3**, a small amount of isomeric product—presumably the corresponding out isomer—was detected by GC/MS.

That the titanium-induced cyclization did indeed give the in isomer **3** rather than the alternative out isomer was confirmed by subsequent reactions. Thus, catalytic hydrogenation of **3** over Adams' catalyst proceeded slowly in ether solution to give *in,out*-bicyclo[4.4.4]tetradecane (**2**), which shows six signals in its ^{13}C NMR spectrum and shows two unique one-proton absorptions at δ 2.50 and 0.81 in its ^{1}H NMR spectrum,[8] assignable to the two different bridgehead protons. Since the resonance at δ 2.50 did not appear when the reduction was carried out with deuterium rather than hydrogen, we assign that signal to the outside hydrogen and the signal at δ 0.81 to the inside hydrogen. The unusually high upfield shift of the inside hydrogen is presumably due to anisotropic shielding by nearby C-C bonds.

One of the most intriguing chemical consequences of in,out bicycloalkane geometry is the possibility of intrabridgehead interactions.[3] Treatment of olefin **3** with trifluoroacetic acid in CDCl$_3$ at room temperature yielded a stable solution that showed a broad one-proton singlet at δ -3.5 in its ^{1}H NMR spectrum and contained only three peaks at δ 18.7, 40.8, and 139.3 in its ^{13}C NMR spectrum. When deuterated trifluoroacetic acid was used, the recovered olefin contained 11 deuterium atoms. These data are consistent with the μ-hydrido-bridged structure **8**, in which the inside hydrogen bears a partial *negative* charge and is symmetrically disposed between the two positively charged bridgehead carbons.[9] Confirmation of the assignment as a static hydrido-bridged structure rather than as a pair of rapidly equilibrating degenerate cationic structures was obtained by using the Saunders isotopic perturbation technique.[10] Introduction of a deuterium atom into the cation by treatment of **3** with deuterated fluorosulfonic acid at -92 °C, and observation of the resultant ^{13}C NMR spectrum, indicated a small splitting of the peak at δ 136.7 into two peaks at δ 137.1 and 136.3. Were two rapidly equilibrating structures involved, a much larger splitting would be expected.[10]



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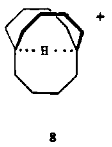

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We are continuing our study of the intrabridgehead chemistry of the *in,out*-bicyclo[4.4.4]tetradecane system.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Experimental section with preparation and spectra of **2** and **3** (2 pages). Ordering information is given on any current masthead page.

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[7] ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.42 (br dd, 1 H), 3.35 (br dd, 1 H) 2.54 (dd, 1 H), 2.34 (q, 1 H), 2.18 (m, 2 H), 2.1-0.85 (m, 18 H); ^{13}C NMR (CDCl$_3$) δ 143.0, 131.7, 36.3, 36.0, 35.1, 33.7, 33.6, 32.3, 29.7, 28.9, 27.5, 26.4, 25.8, 23.1; mass spectrum, m/z M$^+$ 192.

[8] Mp 159-161 °C (sealed tube); ^{1}H NMR (CDCl$_3$) δ 2.50 (m, 1 H), 1.73 (dd, 6 H), 1.53 (m, 12 H), 1.13 (dd, 6 H), 0.81 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 36.1, 31.0, 29.7, 28.7, 25.0, 7.7; mass spectrum, m/z M$^+$ 194.

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Convergent, High-Yield, Regioselective Synthesis of Substituted Benzoquinones from Maleoylcobalt Complexes and Alkynes

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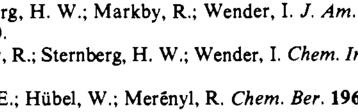
Received June 11, 1984

Treatment of stoichiometric transition-metal carbonyl reagents with alkynes often produces benzoquinones or benzoquinone complexes.[2-15] The generation of these organic products has been rationalized in terms of an initial maleoylmetal complex formation, **1**, followed by subsequent reaction with an alkyne to give a benzoquinone (eq. 1).[16,17] Early work by Maitlis provided strong support for this pathway to quinones.[7] Our studies on the synthesis of analogous phthaloymetal complexes[18,19] and their reaction with



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