Note Added in Proof. Van Gaal and van den Bekerom have published the synthesis of RhX(PCy$_3$)$_2$ (X = F, Cl, Br, I; Cy = cyclohexyl) deduced to be three-coordinate by NMR in the case of the fluoride and deduced to be in equilibrium with a four-coordinate dimer in the case of the chloride: H. L. M. van Gaal and van den Bekerom, *J. Organomet. Chem.*, **134**, 237 (1977).

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(8) Distortion from trigonal planarity toward a T shape splits the d$_{xy}$ and d$_{x^2-y^2}$ energy levels.^{2}
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Strained Ring Systems. 17.^{1}
An Unusual Inversion of Configuration in the Alkali Metal Promoted Protio-Dechlorination of 1,4-Dichloro-*endo*-2-alkoxybicyclo[2.2.0]hexanes to *exo*-2-Alkoxybicyclo[2.2.0]hexanes

Sir:

We wish to report the unique alkali metal promoted protio-dechlorination reductions of 1,4-dichloro-*endo*-2-methoxybicyclo[2.2.0]hexane (**1**)^2 in Li/*tert*-BuOH/THF

1, R = CH$_3$ **2**, R = CH$_3$
3, R = C$_2$H$_5$ **4**, R = C$_2$H$_5$
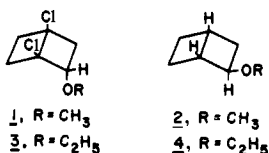
to *exo*-2-methoxybicyclo[2.2.0]hexane (**2**, 100%) and 1,4-dichloro-*endo*-2-ethoxybicyclo[2.2.0]hexane (**3**) in Na/NH$_3$/Et$_2$O (−33 °C) to the *exo*-ethoxy derivative **4** in 93%.^{3} The reduction of **1** was carried out under reflux with excess

Table I. Results of the Reductions of **1** and **3** with a Deficiency of Sodium in NH$_3$/Et$_2$O^a at −33 °C

Mole ratio of sodium/ dichloro compd	% recovered **1** or **3**^{b}	% **2** or **4**^{b}	% adduct **7**^{c}	% polymer^d
Na/**1** (~2/1)^{e,f}	28	56 (**2**)	2 (R = CH$_3$)	14
Na/**3** (~1.2/1)^{g,h}	50	39 (**4**)	7 (R = C$_2$H$_5$)	4

^{a} 300 mL each of NH$_3$ and Et$_2$O. ^{b} By ^{1}H NMR integration vs. an internal standard. ^{c} By ^{13}C NMR. ^{d} By weight. ^{e} 18.2 mmol of **1**. ^{f} 20 mL of cyclopentadiene injected into reaction mixture 5 s after **1** was syringe injected. ^{g} 24.6 mmol of **3**. ^{h} Same as f with only 2–3-s delay in the injection of cyclopentadiene after **3** was added.

lithium wire for 1 h (reduction appeared to be complete in ~0.5 h). Approximately 4 equiv of lithium were consumed. Ethers **2** and **4** were readily identified from their ^{1}H NMR signals of C$_2$ endo-H observed as broadened triplets (**2**, $\delta_{TMS}^{CDCl_3}$ 3.99; **4**, $\delta_{TMS}^{CCl_4}$ 3.99) due to virtual coupling as seen in the exo alcohol (**2**, R = H).^{4} The ^{1}H NMR pattern of this proton was very different from those seen in the endo alcohol^{5a} and certain esters,^{5b} **1**,^{2} and 4-chloro-*endo*-3-methoxybicyclo[2.2.0]hexane-1-carboxylic acid.^{2}

The question of which ring centers were involved in the apparent overall inversion of configuration at C$_2$ in the **1** → **2** and **3** → **4** conversions was answered by carrying out the reduction of **1** in the presence of *t*-BuOD (98% deuterium). The product was **2**-*1,4-d$_2$* containing ~96% deuterium at each bridgehead position.^{6} *The important point here is that no alteration at C$_2$ occurred in the reduction of* **1** *to* **2**, which is assumed to apply to the **3** → **4** reduction also.

Since the olefin bicyclo[2.2.0]hex-1(4)-ene (**5**) is known to be produced by certain chemical and electrochemical reductions of 1-bromo-4-chlorobicyclo[2.2.0]hexane,^{8} several attempts were made to trap the corresponding 2-alkoxy olefins **6** derived from **1** and **3**. **1** was allowed to react with Li wire in triglyme at 70 °C and 50 mm pressure^9 (**2**, bp 57 °C (58 mm)). A cooled trap containing the highly reactive Diels–Alder diene, 2,5-diphenyl-3,4-benzofuran, in THF was placed between the reaction mixture and the pump. After several hours, no evidence of olefin **6** (R = CH$_3$) as an adduct was found in the trap. Addition of *t*-BuOH to the deep blue reaction mixture after this time (Li wire still present) produced a small amount of **2** and a major amount of a polymer.

In separate experiments, **1** or **3** was injected into a solution of Na in NH$_3$/Et$_2$O at −33 °C followed shortly thereafter (2–5 s) by rapid syringe addition of a large excess of 1,3-cyclopentadiene.^{10} In both experiments a deficiency of Na was present so as not to completely convert **1** → **2** and **3** → **4**. The results are given in Table I.

The presence of adduct **7** (R = CH$_3$) was deduced from the ^{13}C NMR spectra of the reaction mixture (after workup) and when much of **2** had been removed by distillation. The larger amount of adduct **7** (R = C$_2$H$_5$) in the limited reduction of **3**

6   **7a**   **7b**
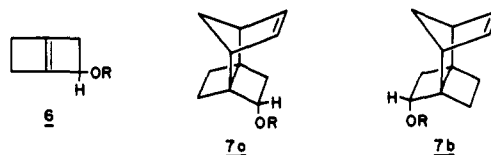
(Table I) allowed for its separation and collection of GLC. This collected sample (containing a small amount of **3**) exhibited the following spectral data: ^{1}H NMR $\delta_{TMS}^{CDCl_3}$ 6.25 (m, 2), 4.27 (octet, C$_7$ H), 3.38 (q, OCH$_2$CH$_3$), and 2.8–1.0 (m, 10); ^{13}C NMR in agreement with **7**;^{11} mass spectrum (heated inlet) *m/e* 190 (M$^+$). The adduct is a single isomer of 7- (**7a**) and 10-ethoxytetracyclo[4.2.2.1^{2,5}.0^{1,6}]undec-3-ene (**7b**) as judged from both GLC and the ^{13}C NMR spectrum. While we assume the stereochemical orientation of the alkoxy group to be exo

Scheme I
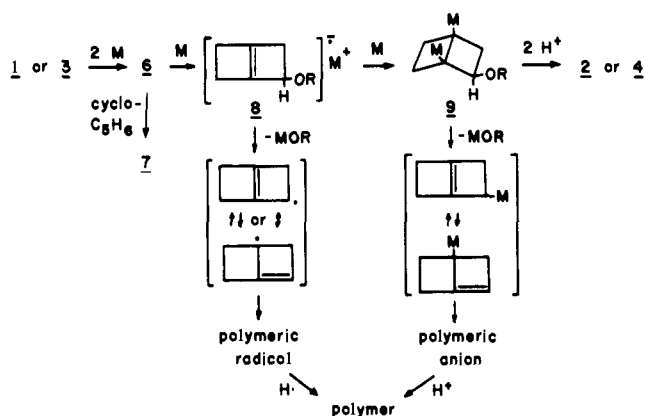
from Diels–Alder reaction of olefin **6** with 1,3-cyclopentadiene, we have no explanation for the apparent specificity in forming only one of the isomers of **7**, and we are unable to establish which isomer (**7a** or **7b**) we have. We also wish to point out that no dimeric products were observed in our Na/NH$_3$ reactions, unlike the analogous reductions of 1-Br-4-Cl[2.2.0].[8d,10]

From the facts that sodium was weighed to ±0.1 g and the expected errors in determining the percentages of the components from the limited reductions of **1** and **3** in Table I, it is difficult to precisely express the number of electrons used in producing each product. Assuming that two electrons are involved in forming olefin **6** which yields adduct **7**, and four electrons effect the **1 → 2** and **3 → 4** conversions, two or three electrons may be used to form the polymer. That this insoluble polymer is not the simple result of olefin polymerization of **6** is evidenced by the *absence* of –OCH$_3$ in its infrared spectrum (KBr pellet).

Reaction of **1** with lithium (∼4 equiv consumed) in THF under reflux for 3 h gave a deep blue solution. Filtration (to remove excess Li) through glass wool with N$_2$ or Ar pressure and quenching with *t*-BuOH led to rapid loss of the blue color and precipitation of a light yellow polymer; no **2** could be found. Some "low molecular weight" material (containing a small amount of **1**) was removed from the polymer by heating it in CCl$_4$. The (^{1}H and ^{13}C) NMR and IR spectra of this CCl$_4$ soluble material (**1** removed) showed the *absence* of –OCH$_3$, >C–OR, >CH–CH$_3$, and >C–CH$_3$ groups, but did indicate some vinyl absorptions.

The ESR spectrum of the filtered blue solution in THF showed only a weak broad signal. Addition of oxygen immediately produced a yellow solution exhibiting an ESR signal attributed to O$_2^-$·.[12] The ^{13}C NMR spectrum of the blue solution (THF) showed only a small amount of unreacted starting material **1**. These spectral data indicate that the species in the blue solution is polymeric and the reaction with O$_2$ (→ O$_2^-$·) show it to be carbanionic in character although the presence of some paramagnetic sites cannot be discounted.

A mechanistic scheme which accommodates the above results is given in Scheme I. This suggests that three electrons are used to produce the polymer in the reductions of Table I by eliminating MOR from the olefin anion radical **8**. The stereospecificity in yielding **9** with exo C$_2$OR is attributed to the expected thermodynamic preference of exo vs. endo,[13] and the probable M · · OR through-space bonding. Since excellent yields of **2** and **4** are produced with no polymer formation in both media with excess alkali metal, the reduction of **8 → 9** must be considerably faster than the intramolecular elimination of MOR from radical anion **8**. This also accounts for the relatively large amounts of **2** and **4** formed in the experiments listed in Table I.

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(6) The deuterium analysis was accomplished by measuring peak areas relative to that of the OCH$_3$ methyl in the proton decoupled ^{13}C NMR spectra of **2** and **2**-*1,4-d$_2$*. No other absorptions interferred in this analysis; however, this appears to be about the lower limit of proton which can be reasonably observed at these bridgehead positions by this method. The mass spectrometric[7] and NMR analyses of **2** and **2**-*1,4-d$_2$* show good agreement and will be discussed in the full paper of this research.
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(9) A quantitative yield of **2** from **1** is obtained in this solvent using either *t*-BuOH or pinacol as the proton source.
(10) We gratefully acknowledge Professor Wiberg's suggestion of this method of olefin **6** trapping and details of these experiments applied to olefin **5** from the Ph.D. thesis of M. Jason where a 30-s time delay of cyclopentadiene addition was used.
(11) The ^{13}C NMR spectrum of adduct **7** will be given in the full paper describing a new synthesis of bicyclo[2.2.0]hexan-exo-2-ol.[4]
(12) We thank Professor W. C. Danen for this spectral determination.
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New Synthetic Reagents. Methylthiomaleic Anhydride: A Synthon for Protected Carbomethoxyketene

Sir:

β-Keto esters are among the most important synthetic intermediates for elaboration of complex molecules. Normally they are prepared by carboxylations of ketones;[1] more recently, alkylations of dianions of simple β-keto esters make more complex ones available.[2] α-Methylene ketones are also valuable intermediates. Most noteworthy is the recent development of a new annulation procedure based upon these compounds.[3] We wish to report an annulative approach to these intermediates employing a new reagent, 2-methylthiomaleic anhydride (**1**), as represented by eq 1. This study also illustrates the utility of sulfur in controlling regiochemistry of dienophiles.[4]

(1)
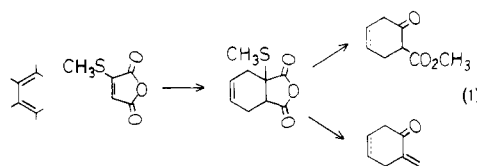
The reagent is prepared by addition of excess methanethiol to acetylenedicarboxylic acid (ethanol, 25 °C),[5] which gives a 6:1 ratio of 2-methylthiofumaric and maleic acids, followed by dissolving in thionyl chloride (*caution:* vigorous evolution of gas) and stirring at room temperature for 1 h and 60 °C for 7 h.[6] Removal of excess thionyl chloride by heating at 120 °C at aspirator pressure (drying tower) and distillation of the residue at 123–125° (0.5 mm) gives the crystalline anhydride,[7a-c] mp 36–37 °C (ether), in 68–77% yields: IR 1845, 1745, 1565 cm^{-1}; ^{1}H NMR δ 6.28 and 2.56; ^{13}C NMR 162.43,