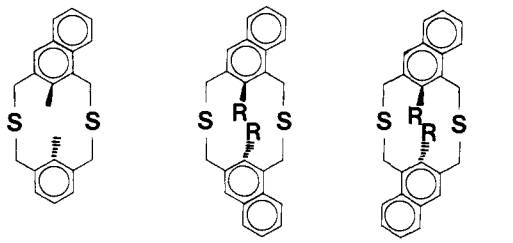

5 6a R=CH_3 b R=H 7a R=CH_3 b R=H

and a mixture of **6a** (mp 290–292 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 8.4–7.3 (m, 10 H, ArH), 4.5–3.4 (m, 8 H, $-CH_2-$), and 1.0 (s, 6 H, $-CH_3$)) and **7a** (mp 296–298 °C; ^{1}H NMR δ 8.4–7.3 (m, 10 H, ArH), 4.25 and 3.6 (AB q, 4 H each, $-CH_2-$) and 1.1 (s, 6 H, $-CH_3$)), respectively. These assignments could be unambiguously made by comparison with spectra obtained for the analogous compounds with internal hydrogens **6b** and **7b** which at the end of the sequence described below gave known dibenzopyrenes. In each case the cyclization also yielded some *syn*-methyl isomers (readily distinguishable by their ^{1}H NMR spectra since the internal methyl protons appear at δ 2.6). Separation was achieved by fractional crystallization and chromatography on silica gel.

When the *anti*-cyclophanes were subjected to a Wittig rearrangement–Hofmann elimination sequence,[9] the highly colored dihydropyrenes **2–4** were obtained directly, in 50–80% yields; no trace of the photoisomers were present. The physical properties and ^{1}H and ^{13}C NMR spectra are listed in Table I. All three compounds appear to be stable in the solid state; however, chlorocarbon solutions decompose fairly rapidly (**3** > **4** > **2**) even at −20 °C in the dark.

The magnetic resonance data are astoundingly clear and support the hypothesis that equivalent Kekulé structures lead to stronger diatropism. Simple ring-current theory[10] would predict similar shieldings for the internal methyl protons of **1–4** based on the peripheral current. In practice, however,[11] benzannelation of conjugated macrocyclic systems (with the exception[2] noted above) has always led to a marked reduction in diatropicity of the large ring. Clearly, for compounds **2** and **3**, which do not possess equivalent Kekulé structures, this is true here, where both the internal methyl protons and internal carbons become progressively less shielded in the series **1** → **2** → **3**. Compound **4**, however, which has two sets of equivalent Kekulé structures, shows almost the full ring current expected, with both the internal methyls and bridge carbons almost as shielded as in **1**, and is probably better considered a macrocyclic annulene than a bisbenzannelated dihydropyrene. This in our view clearly shows the importance of Kekulé structures to macrocyclic systems. Recently several theoretical papers have appeared[12] on the use of Kekulé structures. It will be interesting to see if the theoreticians can concur with our results.[13]

Acknowledgment. We thank the National Research Council of Canada and the University of Victoria for financial support.

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(8) The structure of all new compounds were fully supported by mass and NMR spectral data and elemental analysis.
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(13) This work was presented as a paper at the Third International Symposium of Novel Aromatic Compounds, San Francisco, Calif., Aug 22–25, 1977, where Dr. W. C. Herndon has pointed out that qualitative agreement with our results can be obtained using π-bond orders. Dr. V. Boekelheide also has informed us that his group has obtained similar results in the hexahydrocoronene series.

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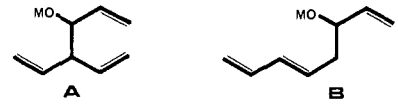
Deep-Seated Rearrangement in the Anionic Oxy-Cope System. Extremely Facile Epimerically Unfavorable Anionic Oxy-Cope Rearrangement of Anti-Bisallylic 1,5,7-Triene Alkoxides[1]

Sir:

In recent years, much attention has been focused on sigmatropic rearrangements[2,4] of anionic oxy-Cope systems which represent substantial improvements in rate and yield relative to the neutral counterparts.[2,4,5] Nevertheless, there still remain some ambiguities concerning the mechanism and the versatility. We wish to report here [1,3]-, [1,5]- and [3,3]-sigmatropic rearrangements of 1,5,5′-[6] and *anti*-bisallylic 1,5,7-triene alkoxides (A and B) incorporated within tricyclic homotropilidenes **2** and **3**, respectively. These observations



A B

would provide not only the wider versatility of an anionic oxy-Cope process but also some insight into the mechanism of formally induced [1,3]-sigmatropic rearrangements in the oxy-Cope related systems.[7] One of intriguing features is the first example of the epimerically unfavorable anionic oxy-Cope rearrangement[8] of **3** which represents sharp contrast to thermal behavior of anti-bisallylic 1,5-diene alkoxides of 2-*exo*-vinyl-2-*endo*-hydroxybicyclo[2.2.2]oct-5-ene (**1**)[2] which is reported not to undergo any sigmatropic rearrangement even after heating at 66 °C for 24 h.

When the vinylcarbinol **2** (M = H, mp 44 °C)[9] was heated with NaH in refluxing tetrahydrofuran (THF), **2** disappeared completely within 3 h with a half-life of 2280 s at 66 °C and, upon quenching with water, 4-hydroxytricyclo[5.3.2.$0^{4,8}$]-dodeca-2,9,11-triene (**7**, mp 77 °C) was obtained quantitatively as the sole product (Scheme I). The structure of **7** was established by the spectral characteristics[11] and chemical evidence that symmetrical hydrocarbons (**9** and **10**)[12,14] were derived from **8**. The potassium alkoxide **2b** (M = K), on the

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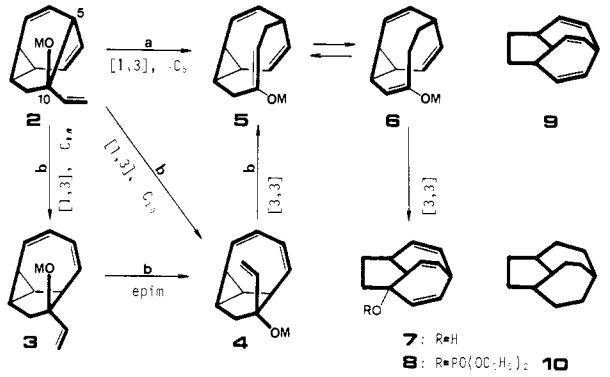
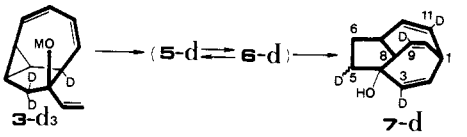
Scheme I



other hand, rearranged much more rapidly to **7** with a calculated half-life of 22 s at 66 °C. Furthermore, an additional 380-fold rate acceleration was obtained upon addition of 18-crown-6[15] and **2b** rearranged to **7** completely within a few minutes at 20 °C. A calculated half-life at 66 °C is 0.06 s in the presence of 6 equiv of 18-crown-6. First-order rate constants for the rearrangement of **2b** to **7** gave linear Arrhenius plots and activation parameters, E_a = 19.5 ± 0.4 kcal/mol, log A = 11.1 ± 0.2 s^{-1} (8.8 to ~34.0 °C) for **2b** and E_a = 14.2 ± 0.5 kcal/mol, log A = 10.1 ± 0.5 s^{-1} (−38.1 to ~−15.5 °C) for **2b** with 6 equiv of 18-crown-6, were obtained.

To account for the rearrangement of **2** to **7**, two formal mechanisms, path a (**2** → **5** ⇄ **6** → **7**) and path b (**2** → **3** and **4** → **5** ⇄ **6** → **7**), can be proposed (Scheme I). Both pathways involve an intermediate **5** which is expected to be in equilibrium[2] with an isomeric enolate **6** under the condition employed. Enolate **6** which has two sets of a *cis*-divinylcyclopropane function should undergo a rapid [3,3]-sigmatropic rearrangement to afford **7**. The most crucial step, however, is a formal [1,3]-sigmatropic rearrangement[16] of **2** to **5**. A direct [1,3]-sigmatropic rearrangement of **2** to **5** in path a would be difficult to discriminate from a sequence of [1,3]- and [3,3]-sigmatropic rearrangements (**2** → **4** → **5**) in path b if **4** rearranges to **7** too rapidly to accumulate during the rearrangement of **2**. It would be, however, conceivable that the formation of **4** should compete with one of an exo isomer **3** when the C_{10} carbon migrates suprafacially to the ring allylic framework. If so, **3** must be another reactive intermediate and rearrange much faster than **2** to **3**. In order to investigate the proposed mechanism, 8-*exo*-vinyl-8-*endo*-hydroxytricyclo[5.3.-0.$0^{2,10}$]deca-3,5-diene (**3**)[19] and its 7,9,9-trideuterio analogue **3**-d_3 were independently synthesized from tricyclo[5.3.0.$0^{2,10}$]deca-3,5-dien-8-one[20] and the stereochemical assignment to **3** was derived from pseudo-contact ^{1}H NMR spectra[19] using Eu(fod)$_3$.[21] Surprisingly, it was found that the alkoxides (**3a** and **3b**, M = Na and K) rearranged cleanly to **7** much faster than **2** to **7**. For instance, the rearrangement of the sodium alkoxide **3a** was completed within 2 h at 24.5 °C, while the potassium alkoxide **3b** rearranged within a few minutes even at 0.8 °C. Furthermore, competition experiments of **3a** and **2a** at temperatures of 24.5 and 34.5 °C showed neither accumulation nor disappearance of **2a** even after the complete conversion of **3a** to **7**. The relative ratio of disappearance of **3a** to **2a** was found to be 140:1 at 42.5 °C. Although these observations do not necessarily exclude the participation of a direct [1,3]-sigmatropic pathway of **2** to **5**, a plausible mechanism for the rearrangement of **2** to **7** could involve **3** and **4** as the possible intermediates.

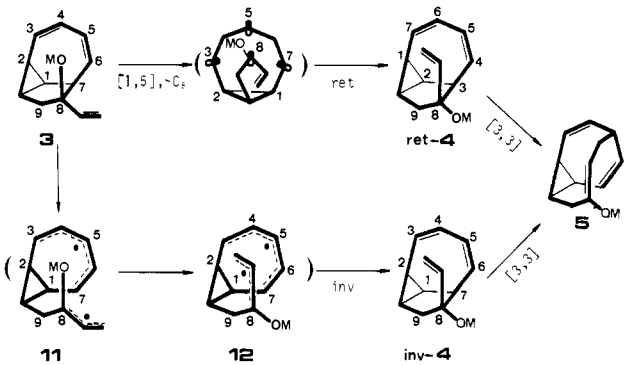
The labeling experiment, on the other hand, clearly proved the intermediacies of **5** and **6**. Thus, the spin decoupling and pseudo-contact ^{1}H NMR spectra[22] of **7**-*d* obtained from **3**-d_3 (M = K) indicate the deuterium distribution at the endo and exo positions of C_5, C_3, C_9, and C_{11} positions. Integrations of



the magnetic resonance signals appearing in pseudo-contact ^{1}H NMR spectra provide hydrogen intensities at all the positions as follows: C_1 H and C_7 H, 2.0 H; C_2 H and C_{10} H, 1.98 H; C_3 H, 0.33 H; C_4 OH, 1.0 H; exo C_5 H, 0.81 H; endo C_5 H, 0.81 H; exo C_6 H, 1.0 H; endo C_6 H, 1.0 H; C_8 H, 1.02 H; C_9 H, 0.51 H; C_{11} H and C_{12} H, 1.55 H. This result is explained by the mechanism in Scheme I since deuteriums at the expected positions of **7** were lost to some extent at the C_3 and C_5 positions, i.e., 33 and 81%, respectively, in enolate equilibration between **5** and **6**.

For the facile Cope rearrangement of the *exo*-vinyl alkoxides **3** to **5**, two mechanistic interpretations can be considered (Scheme II). One is a thermally allowed concerted [1,5]-sig-

Scheme II



matropic rearrangement of **3** to *ret*-**4** with retention of configuration prior to the ordinary Cope rearrangement of *ret*-**4** to **5**. Another path involves, perhaps, a diradical **11**[23] which can afford *inv*-**4** by rotation around the C_8–C_9 bond, followed by reclosure. Then, the ordinary Cope rearrangement of *inv*-**4** can afford **5**. Although *ret*-**4** and **5** can be also afforded directly from diradicals **11** and **12**, the rotation in **11** would be sterically disadvantageous and ring closures in diradicals giving *ret*-**4**, *inv*-**4**, and **5** should compete with the ring closure between the C_5 and C_8 to give a "non-Cope" product **2** as often observed in epimerically unfavorable Cope rearrangements.[8,25] From these aspects, together with evidence that **3** rearranges to **7** without the formation of **2** much faster than **2** to **7**, the reaction path via the concerted [1,5]-sigmatropic epimerization of **3** to *ret*-**4** seems to be more favorable. Thus, the facile rearrangement of anti-bisallylic 1,5,7-triene alkoxides would promise a wider application for two-carbon extention reaction in an appropriately designed system which can epimerize via a [1,5] shift even though that system rejects sterically restricted endo addition of the vinylmagnesium Grignard reagent.

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(11) ν_{max}^{KBr} 3350, 1650, 1400 cm^{-1}; *m/e* 174 (M^+), 159, 145, 132, 117, 103, 91, 89 (100%); ^1H NMR (δ, ppm, $CDCl_3$) 2.97 (C_1, d of t, J = 9.0, 9.0, 10.0 Hz), 6.01 (C_2, dd, J = 9.0, 11.0 Hz), 5.59 (C_3, dd, J = 1.5, 11.0 Hz), 1.40–2.40 (C_5, C_6, m), 2.80 (C_7, C_8, m), 5.76 (C_9, ddd, J = 1.5, 8.0, 9.0 Hz), 6.46 (C_{10}, dd, J = 9.0, 10.0 Hz), 5.88 (C_{11}, dd, J = 9.0, 12.0 Hz), 5.52 (C_{12}, dd, J = 5.0, 9.0 Hz) (by the simultaneous irradiation of three methine hydrogens at the C_1, C_7, and C_8 positions, all of the olefinic hydrogens become doublets at the designated positions); ^{13}C NMR (δ, ppm, $CDCl_3$), 127.2 (d), 129.3 (d), 132.8 (d), 136.2 (d), 136.5 (d), 142.7 (d) (C_2, C_3, C_9, C_{10}, C_{11}, C_{12}), 79.0 (s) (C_4), 36.1 (d), 39.0 (d), 50.0 (d) (C_1, C_7, C_8), 31.7 (t), 42.4 (t) (C_5, C_6).
(12) **9** was obtained in low yield by the lithium–ethylamine reduction[13] of **8**: ^1H NMR (δ, ppm, $CDCl_3$) 3.00 (C_1, dd, J = 8.0, 9.0 Hz), 5.90 (C_2, C_{11}, dd, J = 8.0, 11.0 Hz), 5.59 (C_3, C_{12}, dd, J = 5.0, 11.0 Hz), 2.65 (C_4, C_7, m), 1.5–2.0 (C_5, C_6, m), 2.65 (C_8, m), 5.78 (C_9, dd, J = 8.5, 10.0 Hz), 6.40 (C_{10}, dd, J = 9.0, 10.0 Hz).
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(16) The mechanistic interpretation of a formal [1,3]-sigmatropic rearrangement of an oxy-Cope related system often differs. For instance, in thermal rearrangement of 7-propenyl-7-methoxynorbornenes to 4-*endo*-methyl-2-methoxybicyclo[3.2.0]nona-2,6-diene, Berson[17] proposed a sequence of [1,3]- and [3,3]-sigmatropic rearrangements to account for high stereospecificity of the rearrangement, whereas Fukui's proposal, a multicyclic interaction effect,[18] rather suggests a direct concerted [1,3]-sigmatropic rearrangement which does not require any intermediate. Similarly, the [1,3]-sigmatropic rearrangement[4] reported by Thies and Seitz can also be explained by two intrinsically different mechanisms, i.e., a direct [1,3]-sigmatropic pathway and a sequential [1,3]- and [3,3]-sigmatropic rearrangement which are not discussed about in their report.
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(18) S. Inagaki, T. Minato, H. Fujimoto, and K. Fukui, *Chem. Lett.*, 89 (1976).
(19) $\nu_{max}^{CCl_4}$ 3520 cm^{-1}; ^1H NMR (δ, ppm, $CDCl_3$), 1.4–1.8 (C_1, C_2, C_{10}, m), 6.0–6.2 (C_3, C_4, C_5, m), 3.03 (C_7, dddd, J = 1.5, 1.5, 6.0, 9.0 Hz), 1.19 (endo C_9, dd, J = 3.0, 13.5 Hz), 2.16 (exo C_9, ddd, J = 1.5, 6.5, 13.5 Hz), 6.18 (C_α, dd, J = 11.0, 17.0 Hz), 4.97 (C_β, dd, J = 2.0, 11.0 Hz), 5.25 (C_β,dd, J = 2.0, 17.0 Hz).

Effect of $Eu(fod)_3$ on the ^1H NMR Spectrum of **3** (M = H)

Mol ratio of $Eu(fod)_3$/**3**	$\Delta\delta$, Hz			
	C_α H	endo C_9 H	exo C_9 H	C_7 H
0	0	0	0	0
0.038	37	33	28	27
0.079	82	68	58	59
0.173	172	141	114	121
0.377	387	313	244	273
0.565	552	446	364	387

(20) Tricyclo[5.3.0.$0^{2,10}$]deca-3,5-dien-8-one was prepared by irradiation of bicyclo[4.2.2]deca-2,4,7-trien-9-one in benzene: T. Hagiwara, Ph.D. thesis, Tohoku University, Sendai, Japan, 1974.
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(22) The ^1H NMR spectrum (100 MHz) of the product **7**-*d* from **3**-d_3 is complex, unlike **7**, but the simultaneous irradiation of three methine hydrogens at the C_1, C_7, and C_8 positions can simplify the complicated splittings in the olefinic region as follows: C_2 (d + s), C_3 H (d), C_9 H (d), C_{10} H (d + s), C_{11} H (d), C_{12} H (d + s). However, integration of the magnetic resonance signals in this spectrum does not provide accurate hydrogen intensities since signals locate closely. Integration of all the hydrogens was conducted by pseudo-contact ^1H NMR spectra using $Eu(fod)_3$ which were measured in six different mole ratios ($Eu(fod)_3$/**7**-*d*) from 0.121 to 0.975. Similarly, the C_2 and C_{10} hydrogens and the C_{11} and C_{12} hydrogens shift in pairs, respectively. In each spectrum, the magnetic resonance signals were integrated and then hydrogen intensities were corrected as described in this report based on the exo C_6 (1 H) and endo C_8 (1H) hydrogens which do not shift so much, but separate clearly.
(23) The bicyclo[5.1.0]pentadienyl anion derivative **13** could be also considered

13

as a possible intermediate for the rearrangement of **2** to **3**, but could be ruled out since the bicyclo[5.1.0]pentadienyl anion[24] is reported to be unstable and readily isomerizes to the 1,6-methanoheptatrienyl anion at 0 °C.

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A Mechanism for the Biomethylation of Tin by Reductive Co–C Bond Cleavage of Alkylcobalamins

Sir:

The alkylation of various metals and metalloids by methylcobalamin is a reaction of both mechanistic interest and considerable environmental importance.[1] When the demethylating agent is an electrophile such as Hg^{II}, Tl^{III}, or Pd^{II}, the cleavage has been found to occur by carbanion transfer from cobalt to the attacking metal center.[2-4] More recently the reaction of thiols,[5] or Cr^{II},[6] with alkylcobalamins has been found to occur by reductive homolytic cleavage of the cobalt–carbon bond with alkyl radical transfer. As part of our continuing interest in the bioalkylation of heavy metals, we now present evidence for the alkylation of tin through reductive cobalt–carbon bond cleavage by a species which is generated by one equivalent oxidation of Sn^{II}.

The reaction of methylcobalamin ($\sim 5 \times 10^{-4}$ M) with equimolar aquocobalamin plus a half-fold deficiency of Sn^{II} under N_2 at pH 1.0, in 1.0 M NaCl, was allowed to proceed for 24 h at 20 °C. This reaction was found to follow

$$\underset{}{SnCl_x^{2-x}} + \underset{\text{"base off"}}{CH_3\text{-cob(III)alamin}} + \underset{\text{"base on"}}{H_2O\text{-cob(III)alamin}} \rightarrow CH_3SnCl_y^{3-y} + 2\ \underset{\text{"base off"}}{\text{cob(II)alamin}} + H_2O \quad (1)$$

The product cob(II)alamin was found in 92% yield based on tin. Methyltin was identified by 270-MHz NMR. The CH_3–Sn resonance appeared at 1.01 ppm relative to TSP with detectable satellites for ^1H coupling with ^{117}Sn and ^{119}Sn.[7] Unreacted methylcobalamin and aquocobalamin were found in the ratio 1.3:1. A similar cleavage reaction was found when $FeCl_3$ was substituted for aquocobalamin in the above reaction; however, excesses of Sn^{II} and Fe^{III} over methylcobalamin were necessary to achieve significant cleavage of the cobalt–carbon bond. No reaction was observed between Sn^{II} and methylcobalamin in the absence of an oxidizing agent such as aquocobalamin or Fe^{III}. Catalytic amounts of aquocobalamin, under strictly anaerobic conditions produced no appreciable cleavage.[8] Experiments using ^{14}C-labeled methylcobalamin showed no $^{14}CH_4$, $^{14}CH_3OH$, or $^{14}HCHO$ formation resulting from Sn^{II} cleavage of the cobalt–carbon bond.

The kinetics of the reactions of methyl and ethylcobalamin (2×10^{-5} to 2×10^{-4} M) were investigated at 20 °C in aqueous solutions of hydrochloric acid–sodium chloride with a 10- to 100-fold excess of Sn^{II}. Fe^{III} was added to the reaction mixtures either equimolar or in excess of Sn^{II}. Reactions were followed for 2 to 3 half-lives, when possible, by monitoring the decrease in absorbance at 460 nm for the alkylcobalamin and the concomitant increase in absorbance at 530 nm for the aquocobalamin product.[9] Because of the slow reaction for ethylcobalamin, initial rates were used in this kinetic study. Reactions were found to obey the rate expression

$$-d[B_{12,alkyl}]/dt = k_{obsd}[B_{12,alkyl}] \quad (2)$$

giving good linear plots of $-\ln(A - A_\infty)$ vs. time.[10] Pseudo-first-order rate constants are plotted vs. $[Sn^{II}]$ in Figure 1. In

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