Relationship of the Anionic Behavior of Unsaturated Medium-Ring Alcohols to Structure. Generation and Antarafacial Cyclization of Coiled 8π-Electron Carbanions

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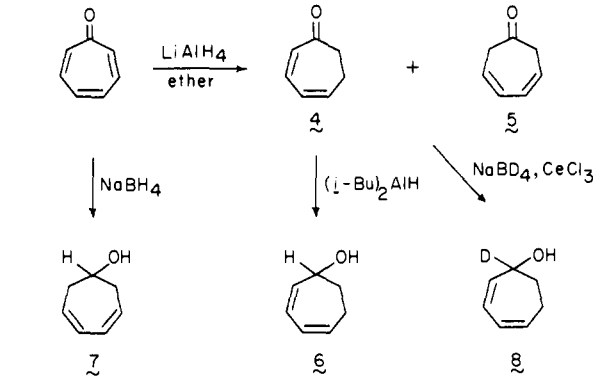
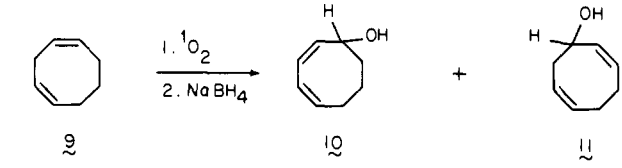
Abstract: The reaction pathways followed by *cis,cis*-2,4-cycloalkadien-1-ols, their 1-alkyl derivatives (**41**), and 1-alkyl-*cis,cis,cis*-2,4,7-cyclononatrien-1-ols (**29**) in neutral and anionic form have been elucidated and, in several cases, subjected to kinetic analysis. It has been found that [1,5]-sigmatropic hydrogen shifts are not as ionically accelerated as [3,3]-carbon rearrangements in these systems (10^6- vs. 10^{10}-fold rate enhancements). Nonetheless, certain processes can be more favored than anionic oxy-Cope rearrangements in certain circumstances. These include 1,3-allylic migration in **29** and dehydration in **41**. The latter reaction may lead to helical, medium-ring trienes that are further deprotonated under the reaction conditions. Subsequent collapse of the 8π-7C intermediates leads ultimately to bicyclo[4.3.1]decadienes (**43**). The relationship of these phenomena to medium-ring conformations is discussed, and additional comparison is made with acyclic conjugated dienols.

Substituent effects have played a pivotal role in mechanistic and synthetic organic chemistry.[1] More recently, substituent alteration within several concerted reactions, e.g., the Diels–Alder and oxy-Cope reactions, has been the subject of considerable mechanistic[2] and theoretical scrutiny.[3] In particular, the fact that a highly ionized alkoxide substituent can substantially accelerate oxy-Cope rearrangements,[4] [1,5]-dienyl hydrogen shifts,[5] [1,3]-sigmatropic carbon migrations,[6] and [4 + 2] cycloreversions,[7] frequently with excellent stereochemical control, has been applied with increasing frequency to synthesis. Particularly notable examples include juvabione,[4b,8] the primary prostaglandins,[5,9] coronafacic acid,[10] multifidene,[11] various germacrane sesquiterpenes,[12] and desmosterol.[13]

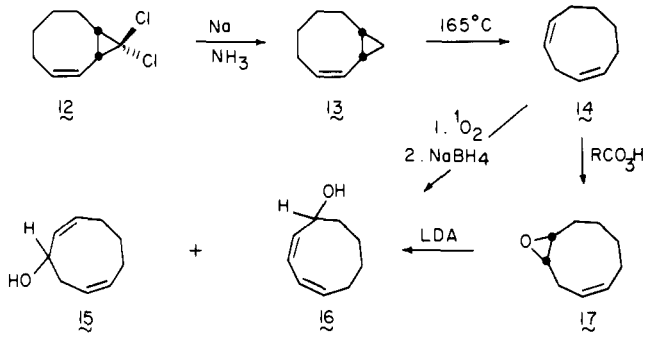
Scheme I



Scheme II



Scheme III



We were attracted to these phenomena when the observation was made in this laboratory that the predilection of neutral **1** for thermal isomerization to **2** via [1,5]-hydrogen sigmatropy could be effectively overridden by conversion to the potassium alkoxide, which rapidly leads only to **3** at room temperature.[5,9,11] This pair

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(3) (a) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1101, 1200, 1206, 1214. (b) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (c) Ahlgren, G. *Tetrahedron Lett.* **1979**, 915. (d) Evans, D. A.; Baillargeon, D. J. *Ibid.* **1978**, 3315, 3319.

(4) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *Ibid.* **1978**, *100*, 2242. (c) Evans, D. A.; Streigerwald, M. L.; Goddard, W. A., III. *Ibid.* **1979**, *101*, 1994. (d) Seebach, D.; Geiss, K.-H.; Pohmakotr, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 437. (e) Miyashi, T.; Hazato, A.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 1008. (f) House, H. O.; Sayer, T. S. B.; Yan, C.-C. *J. Org. Chem.* **1978**, *43*, 2153. (g) Marvell, E. N.; Almond, S. W. *Tetrahedron Lett.* **1979**, 2779. (h) Kahn, M. *Ibid.* **1980**, 4547. (i) Swaminathan, S.; Srinivasan, K. G.; Venkataramani, P. S. *Tetrahedron* **1970**, *26*, 1453. (j) Swaminathan, S.; John, J. P.; Ramachandran, S. *Tetrahedron Lett.* **1962**, 729. (k) Marvell, E. N.; Whalley, W. *Ibid.* **1970**, 509. (l) Wender, P. A.; Sieburth, S. McN. *Ibid.* **1981**, 2471.

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(6) (a) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846. (b) Wilson, S. R.; Mao, D. T.; Jernberg, K. M.; Ezmirly, S. T. *Tetrahedron Lett.* **1977**, 2559. (c) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479. (d) Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 4903. (e) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241. (f) Thies, R. W.; Meshgini, M.; Chiretto, R. H.; Seitz, E. P. *J. Org. Chem.* **1980**, *45*, 185.

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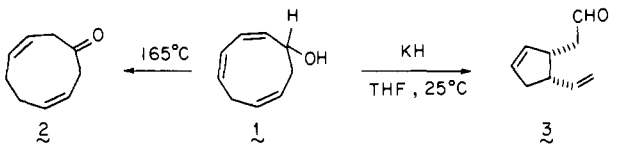

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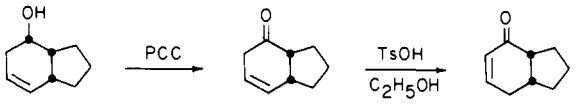
of reactions represented the first example in which the process favored under thermal activation did not continue to dominate under anionic conditions. This intriguing alteration in product distribution made clear the fact that as yet little was known about the manner in which various types of rearrangement pathways were quantitatively affected by oxyanionic substitution. We report herein a general examination of the response of structurally varied alcohols and alkoxides to electronic reorganization. The intent was to explore the relative kinetic ordering of various reaction pathways available to these systems.[14] Although the scope of the present effort has been limited almost completely to medium-ring compounds, several important points have emerged.

Ring-Size Effects in Counterion-Controlled [1,5]-Hydrogen Migration. The Kinetic Bias for [3,3]-Carbon Sigmatropy. In any rearrangement reaction, a fine balance between electronic, steric, and conformational effects is customarily operative. Relevant kinetic data were not available for [1,5]-hydrogen sigmatropy within cyclic dienols. Consequently, **6**, **10**, and **16** were first studied in order that they might serve as suitable points of reference. 2,4-Cycloheptadienol (**6**) was prepared as shown in Scheme I. Following reduction of tropone[15] with lithium aluminum hydride to generate a mixture of **4** and **5** (1:3),[16] isomerization in fluorosulfonic acid according to Childs[17] provided pure **4**. Reduction of **4** with diisobutylaluminum hydride gave **6**, which differed appreciably from isomeric dienol **7** obtained by sodium borohydride reduction of tropone.[18]

cis,cis-1,4-Cyclooctadiene (**9**), prepared from the 1,3 isomer by the method of Moon and Ganz,[19a] was subjected to photooxygenation according to Horinaka's procedure[19b] (Scheme Separation of **10** from the resulting mixture (**10**:**11**, 3:1) was readily accomplished by high-pressure liquid chromatography (HPLC).

The monodichlorocarbene adduct (**12**) of *cis,cis*-1,3-cyclooctadiene may be prepared by reaction with sodium trichloroacetate[20a] in dimethylformamide or by phase-transfer technology. Following reductive dechlorination to **13**, the hydrocarbon was heated to its boiling point (165 °C) to provide *cis,cis*-1,4-cyclononadiene (**14**)[20b] (Scheme III). Target dienol **16** was available admixed with **15** (1:1) upon photooxygenation. This pair of compounds was again separated by HPLC methods. The formation of high levels of unwanted **15** prompted a search for an alternative route to **16**. To this end, **14** was converted to monoepoxide **17**, and the latter was subjected to ring opening with lithium diisopropylamide. Conversion to **16** was slightly improved, but now a second isomeric alcohol containing only one double bond was formed as ca. 40% of the product mixture. This new alcohol was formulated as **18** on the basis of spectral and mechanistic



18 19 20

Table I. Rate Constant and Activation Parameter Data for the Thermal [1,5]-Sigmatropic Rearrangement of 1, 6, 10, and 16

substrate	temp, °C	k, s^{-1}	E_{act}, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	169.5	2.86×10^{-4}	29.9	29.4	32.1	−9.1
		2.79×10^{-4}				
	159.5	1.24×10^{-4}				
		1.14×10^{-4}				
	149.5	1.21×10^{-5}				
		1.19×10^{-5}				
	25.0[a]	1.62×10^{-11}				
6	114.5	4.60×10^{-4}	24.6	24.0	27.7	−12.5
		4.15×10^{-4}				
		4.05×10^{-4}				
	103.0	1.71×10^{-4}				
		1.52×10^{-4}				
		1.42×10^{-4}				
	91.5	6.27×10^{-5}				
		5.64×10^{-5}				
		5.16×10^{-5}				
	25.0[a]	2.87×10^{-8}				
10	117	3.87×10^{-4}	24.8	24.2	28.2	−13.3
		3.53×10^{-4}				
	103	1.13×10^{-4}				
		1.09×10^{-4}				
	91	4.48×10^{-5}				
		3.36×10^{-5}				
	25.0[a]	1.33×10^{-8}				
16	176.5	4.29×10^{-4}	29.0	28.4	31.8	−11.4
		4.24×10^{-4}				
	163.5	1.69×10^{-4}				
		1.63×10^{-4}				
	150	5.95×10^{-5}				
		5.25×10^{-5}				
	25.0[a]	2.94×10^{-11}				

[a] Extrapolated values based upon the activation parameters.

considerations, pyridinium chlorochromate oxidation to unconjugated cyclohexenone **19** (IR 1700 cm^{-1}), and ultimate isomerization to **20** (IR 1665 cm^{-1}) under acidic conditions.

Cope has studied the rearrangement pathways of medium-ring epoxides and has noted that cyclooctene oxide, for example, is readily converted to the bicyclic product upon exposure to lithium diisopropylamide.[21] This outcome was rationalized in terms of a carbenoid intermediate resulting from 1,1 elimination. Although the yield of **16** was not greatly improved over the previous method, the epoxide route proved more simple to carry out on a multigram scale.

When highly purified samples of the three dienols were heated, smooth rearrangement to the respective β,γ-unsaturated ketones[22] was observed. First-order rate constants for these [1,5]-hydrogen shifts, including the conversion of **1** to **2**, afforded linear Arrhenius plots and the activation parameters collected in Table I. To allow suitable comparison, we extrapolated the kinetic data to 25 °C. It can be seen that the ease of [1,5]-hydrogen migration increases as the ring size is decreased. This is the likely result of stereoelectronic alignment of the migrating C–H bond and the $p\pi$ components of the flanking diene moiety. Molecular models indicate that the best orbital overlap in the transition state can be achieved in the case of **6**, with progressive structural inhibition of this alignment as the ring is expanded. The relative rates of [1,5]-hydrogen sigmatropy in **6**, **10**, and **16** are 976, 452, and 1, respectively. Dienol **16** rearranges 1.8 times faster than **1**. The present kinetic data agree well with that previously recorded for other seven- and eight-membered dienes (Table II).

When *cis,cis*-2,4-cyclooctadienol (**10**) was treated with potassium hydride in dry tetrahydrofuran, clean, high-yield conversion to 3-cyclooctenone (post quench) occurred within a short

(14) Two preliminary communications have appeared on this subject: (a) Crouse, G. D.; Paquette, L. A. *Tetrahedron Lett.* **1981**, 3167. (b) Paquette, L. A.; Crouse, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 6235.
(15) Radlick, P. *J. Org. Chem.* **1964**, *29*, 960.
(16) Schuster, D.; Scholnick, B. R.; Lee, F. H. *J. Am. Chem. Soc.* **1968**, *90*, 1300.
(17) Hine, K. E.; Childs, R. F. *J. Chem. Soc., Chem. Commun.* **1972**, 144. *J. Am. Chem. Soc.* **1973**, *95*, 3289.
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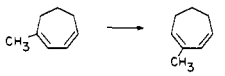
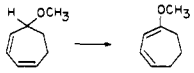
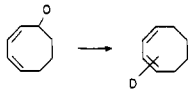
(19) (a) Moon, S.; Ganz, C. *J. Org. Chem.* **1969**, *34*, 465. (b) Horinaka, A.; Nakashima, R.; Yoshikawa, M.; Matsuura, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2095.
(20) (a) Detty, M. R.; Paquette, L. A. *Tetrahedron Lett.* **1977**, 347. (b) Glass, D. S.; Boikess, R. S.; Winstein, S. *Ibid.* **1966**, 999.
(21) Cope, A. C.; Berchtold, G. A.; Peterson, P. E.; Sharman, S. M. *J. Am. Chem. Soc.* **1960**, *82*, 6370. Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev., Chem. Soc.* **1966**, 159.
(22) Heap, N.; Whitham, G. H. *J. Chem. Soc. B:* **1966**, 164.

Table II. Kinetic Data for [1,5]-Hydrogen Sigmatropy

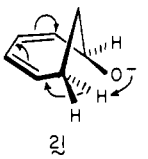
reaction	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	ref
	28.6	−9.9	*a*
	25.7	−15.5	*b*
	25.8	−8.0	*c*
	29.3	−10.0	*d*

[a] Mironov, V. A.; Chizov, O. S.; Kimefield, La. M.; Akhrem, A. A. *Tetrahedron Lett.* 1969, 499. Mironov, V. A.; Akhrem, A. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* 1972, *21*, 1582, 1791. [b] Nozoe, T.; Takahashi, K. *Bull. Chem. Soc. Jpn.*, 1965, *38*, 665. Weth, E.; Dreiding, A. S. *Proc. Chem. Soc., London* 1964, 59. [c] terBorg, A. P.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* 1963, *82*, 1189. [d] See ref 20.

period of time. The response of **16** was entirely analogous. An exception to this trend was the behavior of **6**, which rearranged to a mixture of 3-cycloheptenone and dienol **7**. The relative proportion of these products was temperature dependent such that the ketone dominated at higher temperatures (−15 to +7 °C) while **7** was major at lower temperatures (−24 °C). Quantitative kinetic studies were performed at various temperatures for each system, including **1** (Table III). Rate constants, which were independent of the substrate concentration, established that these reactions adhere to first-order kinetics. Rate constants for the two distinct phenomena that operate in the case of **6** were obtained by dividing the rate of disappearance of the dienol into the ratio of initial rates of product formation.

Comparison of the thermal and anionic data is highly informative. Specifically, we see that, regardless of ring size, the rate of [1,5]-hydrogen migration experiences marked acceleration on the order of 10^5–10^6 when alkoxide rather than hydroxyl is the substituent adjacent to the dienyl moiety. Also noteworthy are the activation parameters. The evident lowering of E_{act} adds support to the argument that the anionic reactions are energetically favored. However, although the $\Delta S^{\ddagger}$ values are appreciably negative in all cases, such data are not considered to be an acceptable criterion for concert in a liquid-state reaction involving ionic, solvated species. Additional criteria must be upheld before synchronous electronic reorganization is confirmed.

The effect of added ion-pair dissociation was investigated by conducting the rearrangements of the potassium alkoxides in the presence of 5 equiv of 18-crown-6. Kinetic measurements, which were conducted at those temperatures most convenient to data acquisition, made available the following rate constants: k (−15 °C) **6**–O^-K^+, 1.46×10^{-3} s^{-1}; k (20 °C) **10**–O^-K^+, 3.81×10^{-4} s^{-1}; k (4.5 °C) **16**–O^-K^+, 2.97×10^{-3} s^{-1}. These results signify that perturbation of the ion-pair structure results in a 9-fold additional rate acceleration. For [3,3]-carbon sigmatropy, this factor is 180.[4a] Under these conditions, **6**–O^-K^+ is converted *only* to 3,5-cycloheptadienol (**7**). This phenomenon presumably arises from an enhanced predilection on the part of the increasingly "naked" alkoxide anion to experience intramolecular hydride transfer as in **21**, owing to the unique geometry of this system.



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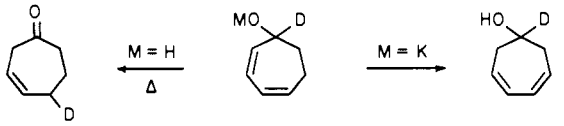
Suitable control experiments revealed that 3-cycloheptenone and 3,5-cycloheptadienol are not interconverted under the reaction conditions. Further, the deuterated alcohol **8**, available from reduction of **4** with sodium borodeuteride admixed with cerous chloride,[23] was converted uniquely to **23** in the presence of KH,



22 **23**

Table III. Rate Constant and Activation Parameter Data for Anionic [1,5]-Sigmatropy in 6, 10, and 16

substrate	temp, °C	k, s^{-1}	E_{act}, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$k_{anionic}/k_{thermal}$(25 °C)
6[a]	0	5.72×10^{-4}	13.8	13.2	20.7	−25.1	1.4×10^5
	−4.5	3.07×10^{-4}					
		2.50×10^{-4}					
	−24	5.31×10^{-5}					
		3.26×10^{-6}					
	25.0[b]	4.0×10^{-3}					
10	5.5	4.08×10^{-4}	15.6	15.1	21.0	−20	1.8×10^5
		3.55×10^{-4}					
	−4.5	1.30×10^{-4}					
		1.26×10^{-4}					
	−15	4.18×10^{-5}					
		3.88×10^{-5}					
	25.0[b]	2.39×10^{-3}					
16	54	6.25×10^{-4}	14.7	14.1	23.1	−30.3	2.3×10^6
		5.65×10^{-4}					
	41	2.64×10^{-4}					
		2.61×10^{-5}					
	28	8.76×10^{-5}					
		8.19×10^{-5}					
	25.0[b]	6.87×10^{-5}					
6[c]	0	1.71×10^{-4}					
	−4.5	1.99×10^{-4}					
		1.96×10^{-4}					
	−24	6.18×10^{-5}					

[a] Rate data apply only to 3-cycloheptenone production. [b] Extrapolated values based upon the activation parameters. [c] Rate data apply only to formation of 7.

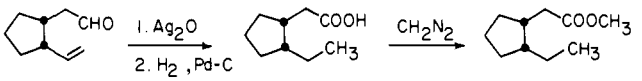
Table IV. Rate Constant and Activation Parameter Data for Anionic Oxy-Cope Rearrangement of 1 and 15[a]

substrate	temp, °C	k[3,3], s^{-1} [b]	E_{act}, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1, K^+ salt	15	6.62×10^{-4}	15.4	14.8	21.3	−21.7
	5	2.52×10^{-4}				
	−3.5	1.05×10^{-4}				
	25.0[c]	1.63×10^{-3}				
1, Na^+ salt	66	5.3×10^{-4}				
1, Li^+ salt	66	too slow to measure				
15, K^+ salt	25	6.1×10^{-4}				

[a] Anhydrous tetrahydrofuran was employed as solvent in all runs. [b] Average value derived from duplicate runs. [c] Extrapolated value based upon the activation parameters.

irrespective of whether or not 18-crown-6 was present. The usual deuterium isotope effects sufficiently retard the migration of deuterium to cause clean conversion to **23** to prevail. On heating **8** in carbon tetrachloride, **22** was formed exclusively.

Quantitative kinetic measurements involving **1**–O^-K^+ and the structurally related dienoxide **15**–O^-K^+ are summarized in Table IV. The latter compound underwent isomerization to give only aldehyde **24**. The structure of this disubstituted cyclopentane



24 25 26

was established by conversion to **26**, the stereochemistry of which had been established in earlier work by Crouse.[24] For **1**, therefore, the rate acceleration accompanying anionic oxy-Cope rearrangement is 2.4×10^{10}, an order of magnitude in agreement with precedent.[4] Consequently, the general effect of oxy substitution on neighboring-center chemistry is seen to be substantial, although appreciably less so for [1,5]-hydrogen migration than for [3,3]-carbon sigmatropy.

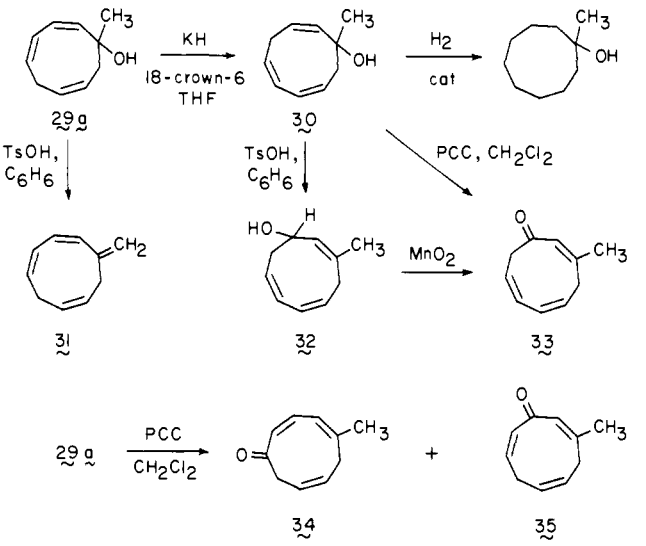
Anionic Behavior of 1-Alkyl-*cis*,*cis*,*cis*-2,4,7-cyclononatrienols. On the basis of the well-established dynamic behavior of *cis*,*cis*,*cis*-1,3,6-cyclononatrienes,[25] one can anticipate that there should be no intrinsic barrier to rapid interconversion of crown conformations **27** and **27′** of 1,3,7-triene congeners at temperatures above

27 27′

0 °C. Different conformational biases should, of course, be adopted as the steric size of R is manipulated. In the parent trienol **1** (R = H), we consider it most plausible that anionic oxy-Cope rearrangement occurs predominantly, if not exclusively, via conformation **27′**, in which the much smaller substituent is positioned in the intraannular cavity. This state of affairs need no longer hold when R becomes methyl or ethyl. Furthermore, [1,5]-sigmatropic shifts become less likely in these alkylated derivatives since carbon atoms are now required to experience migration. For these reasons, the anionic behavior of **29a** and **29b** was next examined.

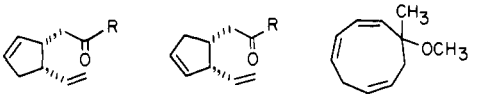
28 29a, R = CH_3; b, R = CH_2CH_3

Scheme IV



When **29a** was treated with potassium hydride and 1.2 equiv of 18-crown-6 in dry tetrahydrofuran at −25 °C, conversion primarily to the isomeric alcohol **30** (86% isolated) was observed to be complete in 2 h (Scheme IV). Catalytic hydrogenation of **30** afforded 1-methylcyclononanol, thereby confirming the intact nature of the nine-membered ring. In contrast to **29a**, which is converted to **31** when allowed to stand with *p*-toluenesulfonic acid in benzene at room temperature, **30** is isomerized to a third cyclononatrienol (**32**) under identical conditions. Authentication of the structural assignments to **30** and **32** was achieved by oxidation. Thus, addition of manganese dioxide to **32** gave rise to **33**, which was also the expected[26] product of pyridinium chlorochromate (PCC) oxidation of **30**. By comparison, PCC oxidation of **29a** afforded a mixture of **34** (57%) and **35** (38%). The three cyclononatrienones could easily be distinguished on the basis of their ^1H NMR and UV spectra. Although ethyl homologue **29b** was not as extenstively investigated, it gave evidence of entirely comparable behavior.

When **29a** was converted to its potassium salt in the absence of 18-crown-6, 3 h was required for the accompanying isomerization to be complete. These conditions led to production of **30** (40% isolated) and an inseparable mixture of **36a** and **37a** (35% isolated), thus revealing that anionic oxy-Cope rearrangement was



36a, R = CH_3; b, R = C_2H_5 37a, R = CH_3; b, R = C_2H_5 38

now competitive with prototropic shifting. When sodium hydride in refluxing tetrahydrofuran was employed, the percentage of dienyl ketones rose to approximately 90%. Isomerically pure samples of **36a** and **37a** were acquired through thermal rearrangement of neutral **29a** and **30**, respectively (see Table V). Again, **29b** exhibited parallel changes in product distribution.

In a parallel series of experiments designed to allow comparative assessment of intra- vs. intermolecular oxyanionic influences, methyl ether **38** was prepared and treated with 2 equiv of potassium ethoxide under conditions in which **39a**–O^-K^+ was completely isomerized. After 3 h at 0 °C, the extent of 1,3-prototropic shift in **38** was only 10%. Although the efficiency of this process could be enhanced by the addition of 18-crown-6 (2 h at −25 °C, ca. 90% conversion), neither set of conditions led to loss of starting material with the rapidity (qualitative studies only) observed in the case of **39a**–O^-K^+.

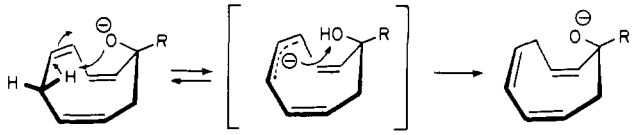
(23) Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2226.
(24) Crouse, G. D. Ph.D. Dissertation, The Ohio State University, 1981.
(25) Paquette, L. A.; Ley, S. V.; Traynor, S. G.; Martin, J. T.; Geckle, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 8162.
(26) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

Table V. Rearrangement Behavior of 1-Methyl-*cis,cis,cis*-2,4,7-cyclononatrienol Derivatives

compound	solvent (additives)	temp, °C	time, h	[3,3]~C/ [1,3]~H
29a-OH	THF	205	2	100:0
29a-O^-Na^+	THF	66	3	~90:10[a]
29a-O^-K^+	THF	0	3	~40:60[a]
29a-O^-K^+	THF (1.1 equiv of 18-crown-6)	−25	<2	0:100
29a-O^-Na^+	THF (2 equiv of $Na^+{}^-CH_2SOCH_3$)	0	1	0:100
38	THF (2 equiv of KOC_2H_5)	0	3	0:100[b]
38	THF (2 equiv of KOC_2H_5; 2 equiv of 18-crown-6)	−25	2	0:100[c]

[a] These values are somewhat inaccurate owing to competing rearrangement of 30-O^-K^+ under the reaction conditions. [b] <10% conversion realized. [c] ~90% conversion realized.

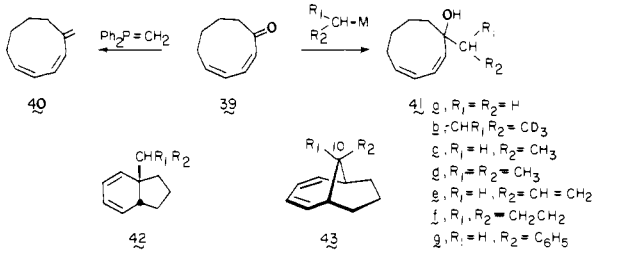
Scheme V



The behavior of the potassium alkoxides of **29a** and **29b** can most logically be rationalized on the basis of the conformational isomerization **27** ⇄ **27′**. The presence of an R substituent bulkier than a proton apparently drives the equilibrium toward **27**, where the alkoxide occupies an endo position on the alicyclic framework. Upon visual inspection of molecular models, the close proximity of negatively charged oxygen to one of the doubly allylic C-6 protons is unmistakable. That abstraction can occur readily as in Scheme V is not surprising. Whether reprotonation is intramolecular as shown or intermolecular is not known. Quenching with deuterium oxide gave no evidence for isotope incorporation (mass spectral analysis), thus ruling out the likelihood of a dianionic species.

The driving force underlying the observed allylic rearrangement appears to be the higher level of pπ conjugation available to the conjugated diene moiety in **30** (λ_{max} 234 nm) relative to that present in **29** (shoulder at 220 nm). Molecular models indicate that **29** is more conformationally strained than **30**, the diene subunit in the former being locked in nearly perpendicular geometry. Under equilibrating conditions (2 equiv of dimsyl anion), in fact, **29a** is totally isomerized to **30** after 1 h at 0 °C.

Mild Base-Promoted Dehydration of 1-Alkyl-*cis,cis*-2,4-cyclononadienols. Attention was next turned to 1-alkyl derivatives of **16**, systems in which neither [3,3]-oxy-Cope nor [1,5]-hydrogen rearrangement can operate. The possibilities for allylic rearrangement also seemed negligible. Nonetheless, the action of potassium hydride in refluxing tetrahydrofuran was adequate to cause methyl derivative **41a** to be entirely consumed in 3 h. The



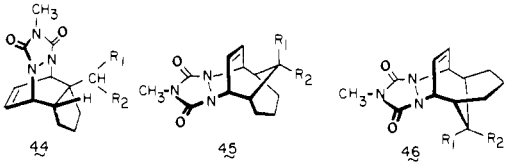
pair of dienes **42a** and **43a**, both of which are dehydration products of the alcohol, were efficiently produced. Major product **42a** ($R_1 = R_2 = H$, 60%) was characterized by a ^1H NMR spectrum featuring a methyl singlet at δ 1.05 and a combination of four vinylic, one allylic, and six methylene protons. A crystalline 1:1 Diels–Alder adduct with *N*-methyltriazolinedione was formed instantaneously at −40 °C. ^1H NMR analysis of this substance showed it to exhibit two methyl singlets (N-CH_3 and C-CH_3),

Table VI. Product Ratios for Anionic Rearrangement of 1-Alkyl-*cis,cis*-2,4-cyclononadienols[a]

compound	conditions	product ratio, **43** vs. **42**
41a	A	40:60
	B	100:0
41b	B	100:0
41c	A	29:71
	B	100:0
41d	A	10:75[c]
	B	68:12[c]
41f	A	0:100[d]
	B	0:100
41g	A	100:0
	B	100:0

[a] Values given are relative percentages determined by VPC analysis; conversions are excellent. Ratios were observed in select cases to be independent of reaction time. [b] Conditions used: were (A) KH, THF, reflux; (B) KH, Et_2O, 18-crown-6, 20 °C. [c] A third product believed to be the 2-isopropyl derivative of **42** (lacking the angular substituent) was also isolated (15–20%). [d] See text for discussion of accompanying ketone formation.

as well as two vinylic (δ 5.8) and two allylic hydrogens (δ 4.7). Upon irradiation of the vinylic proton signal, the allylic protons collapsed to a singlet and a doublet (J = 3.5 Hz). The magnitude of this coupling constant served to indicate that the proton with which the bridgehead hydrogen enjoys spin interaction is oriented exo as in **44a**.[27]



Minor hydrocarbon **43a** ($R_1 = R_2 = H$, 40%) exhibits no methyl peak in its proton NMR spectrum; the presence of a plane of symmetry is apparent from its six-line ^{13}C NMR spectrum. Prolonged reaction with *N*-methyltriazolinedione afforded a 1:1 adduct in which symmetry was retained. These results are consistent with the formation of either **45a** or **46a**. Additional supportive evidence was gained upon catalytic hydrogenation of **43a**, which gave bicyclo[4.3.1]decane, mp 81 °C, identical in all respects with the reduction product of bicyclo[4.3.1]deca-2,4,6,8-tetraene.[28] The saturated hydrocarbon had been previously prepared by Del Cima and Pietra;[29] spectral comparison established the common nature of the compounds.[30] However, the incongruity of their melting point (97 °C) and ours cannot be explained.

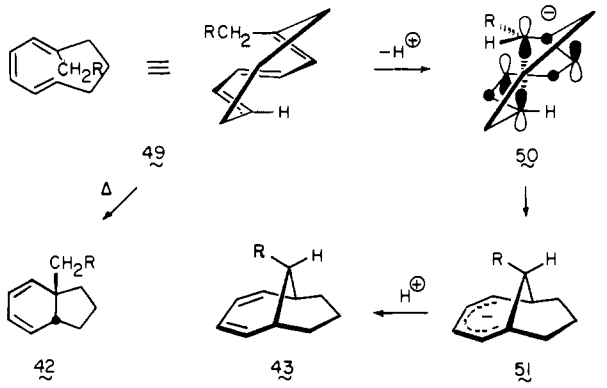
Coaddition of 1.1 equiv of 18-crown-6 to the mixture of **41a** and potassium hydride caused an appreciable rate enhancement. Not only was dehydration complete in 2–3 h at room temperature, but **43a** was the only reaction product!

The ethyl (**41c**) and isopropyl derivatives (**41d**) behaved in analogous fashion (Table VI), although the **42**:**43** ratio did increase somewhat in proportion to the added substitution. The absence of isomers at C-10 in the bicyclo[4.3.1]decadienes is noteworthy. The syn configuration of the methyl group in **43c** ($R_1 = CH_3$, R_2 = H) is assigned on the basis of its shielded nature (d at δ 0.85, J = 7 Hz). For comparison, the two methyl singlets in **43d** ($R_1 = R_2 = CH_3$) appear at δ 1.20 and 0.98. The unreactivity of **43c** and **43d** toward *N*-methyltriazolinedione provides less direct evidence that steric congestion has appeared above the diene surface.

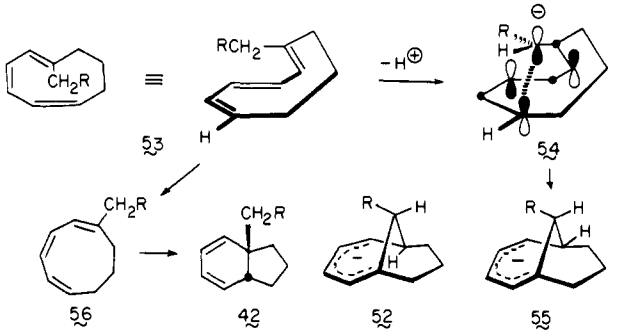
The fate of deuterated dienol **41b** ($CHR_1R_2 = CD_3$) under the same conditions proved rather ambiguous, the isolation of mono-

(27) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724.
(28) Rajan Babu, T. V.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 8261. We thank Professor Shechter for a sample of bicyclo[4.3.1]deca-2,4,6,8-tetraene.
(29) Del Cima, F.; Pietra, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1710.
(30) The chemical shifts given in the original Italian report[29] are doubled because the authors erred in gauging the sweep width of their recorded spectrum.

Scheme VI



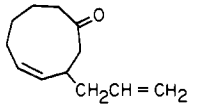
Scheme VII



and dideuterated products (mass spectral analysis) inferring that deprotonation/reprotonation is occurring under the reaction conditions.

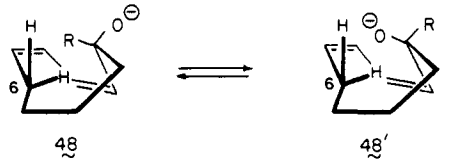
Cyclopropyl derivative **41f** ($R_1R_2 = CH_2CH_2$) was transformed uniquely into **42f** ($R_1R_2 = CH_2CH_2$) under either set of conditions. In contrast, benzyl substitution as in **41g** ($R_1 = C_6H_5$, $R_2 = H$) promoted conversion only to **43g** ($R_1 = C_6H_5$, $R_2 = H$) without regard for the presence or absence of 18-crown-6. Curiously, some side-chain fragmentation was observed under the latter set of conditions, ketone **19** being isolated in 24% yield.

In an effort to compare the facility of the dehydrative process relative to [3,3]-carbon sigmatropy, we prepared and treated tertiary allylic alcohol **41e** ($R_1 = CH{=}CH_2$, $R_2 = H$) with potassium hydride and 18-crown-6 as before. Since ketone **47** proved



to be the major reaction product (<10% of combined dehydration products were found), the oxy-Cope rearrangement is seen to be kinetically dominant.

One rationale for the formation of dehydration products follows from the reactivity patterns observed in the cyclononatrienol series. The unsubstituted cyclononadienyl alkoxide **16**–O^-K^+ presumably reacts via conformation **48** (R = H), which features the smaller substituent in the cleft of the ring and stereoelectronic factors nicely geared to intramolecular [1,5] migration of that hydrogen which is geminal to the negatively charged oxygen. An increase in the steric bulk of R favors a shift in equilibrium from **48** to **48′** and inward orientation of the highly anionic alkoxide sub-



stituent with resultant close proximity to the hydrogens on C-6. Intramolecular proton abstraction can follow, but the intermediate may otherwise choose to expel hydroxide ion and form triene **49** instead of reprotonating as encountered earlier in the trienyl analogue (see Scheme V). Whether this is a concerted or two-step process cannot be determined from the available information. In any event, the hypothetical **49** may experience thermally allowed disrotatory 6π electrocyclization to deliver **42** (see Scheme VI) when the reaction is conducted in refluxing tetrahydrofuran. The all-cis isomer of **49** could also logically account for the formation of **42**,[31] but Dreiding models of **48′** suggest that access to **49** is more kinetically feasible, particularly if the process is intramolecular and concerted. Although **49** is unknown and attempts to isolate this triene have been unsuccessful, theoretical calculations have shown the demethyl *trans,cis,trans*-triene to be only slightly less stable than its all-cis isomer.[32]

An important structural feature of **49** is its coiled geometry, which serves to project the alkyl substituent to the interior of the molecule and above the distal double bond. When sufficiently basic conditions exist (in particular when 18-crown-6 is present), deprotonation to give the coiled 8π-7C carbanion **50** would presumably be facilitated. Acyclic systems of this type are known[33] and have been shown to experience very rapid cyclization to cycloheptadienyl anions at low temperatures. For steric reasons, the deprotonation of **49** should be stereocontrolled to position R away from the trimethylene belt (see **50**). Furthermore, the terminal lobes of this heptatrienyl system are not only geometrically fixed in close proximity but also synphasic in the highest occupied molecular orbital. Hence, there should be little impedance to C–C-bond formation at these terminal positions since the requirement of antarafaciality is clearly met and no additional σ-bond alignment is necessary. We conjecture that if **51** is indeed produced, bridgehead protonation would deliver **43**.

As expected from the preceding mechanistic considerations, an increase in the acidity of the allylic proton caused by R [CH_2Ph > CH_3 > CH_2CH_3 > $CH(CH_3)_2$ ≫ cyclopropyl C–H] favors production of **43** relative to **42**. Additionally, the coiled geometry of **50** is seen to be a prerequisite to electrocyclization as demonstrated by the fact that triene **40** can be recovered intact after submission to the identical reaction conditions.

The chief merit of the mechanism advanced in Scheme VI is utilization of the same *trans,cis,trans*-triene to produce both **42** and **50**. However, close inspection of the **50** → **51** conversion shows that the proposed cyclized carbanion has an "inside" bridgehead proton (see **52**). Consequently, inversion of configuration at this site is required prior to delivery of the final product (**43**).

This possible complication may be bypassed by abstraction of the alternative C-6 proton in **48′** to give *cis,cis,trans*-triene **53** and subsequently anion **54** (Scheme VII). This 8π-7C intermediate is also coiled and enjoys essentially all of the geometric and electronic features attributed to **50**. In this instance, C–C bond formation delivers the bridged carbanion **55**, which is epimeric with **52**. Although this aspect of the mechanistic dilemma is more aesthetically satisfying, it must be recognized that triene **53** cannot lead directly to **42** if orbital symmetry constraints remain in effect. Following double-bond isomerization within **53**, however, disrotatory 6π electrocyclization of the newly formed cis,cis,cis-isomer **56** is feasible, as pointed out earlier. These mechanistic options might prove experimentally differentiable, and studies in this

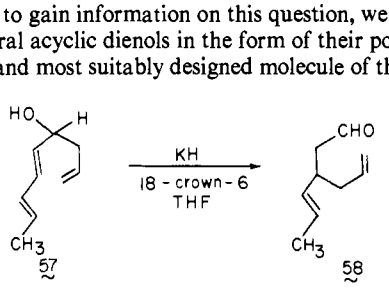
(31) (a) Watthey, J. W. H.; Winstein, S. *J. Am. Chem. Soc.* **1963**, *85*, 3715. (b) Vogel, E.; Grimme, W.; Dinne, E. *Tetrahedron Lett.* **1965**, 391. (c) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3805; **1980**, *102*, 4456.

(32) Buemi, G.; Zuccarello, F.; Grasso, D. *J. Mol. Struct.* **1977**, *42*, 195. Calculations have also been performed on the isomeric [10]annulenes with similar results: Farnell, L.; Kao, J.; Radom, L.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 2147.

(33) (a) Bates, R. B.; McCombs, D. A. *Tetrahedron Lett.* **1969**, 1977. (b) Bates, R. B.; Deines, W. H.; McCombs, D. A.; Potter, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 4608. (c) Marchand, A. P.; Lehr, R. F. "Pericyclic Reactions"; Academic Press: New York, 1977; Vol. I.

direction have been initiated. It is, of course, possible that these reactions may also take a pathway entirely different from the above.

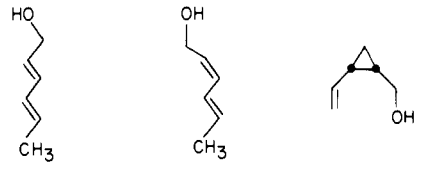
The Behavior of Acyclic Conjugated Dienols. Since entropic effects can be expected to exert a negative impact on sigmatropic behavior in acyclic systems, open-chain compounds should exhibit a greater reticence toward intramolecular bond reorganization. In an effort to gain information on this question, we prepared and heated several acyclic dienols in the form of their potassium salts. In the first and most suitably designed molecule of this series (**57**),



57 **58**

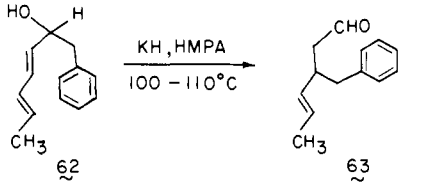
oxy-Cope rearrangement was seen to be complete after several hours in refluxing tetrahydrofuran solution containing 18-crown-6. It is recalled that the analogous conversion of **1** to **3** occurs rather rapidly at room temperature.

The pair of trans double bonds in dienol **59** lock the molecule



59 **60** **61**

into a conformation that is little conducive to concerted [1,5]-hydrogen migration. Not unexpectedly, **59**–O^-K^+ proved stable at temperatures up to 100 °C for prolonged periods of time. The structurally more favorably disposed dienol **60** proved also to be unreactive, even under the most anionic conditions utilized earlier in this study. Similar negative results were recorded in the attempted rearrangement of homodienol **61**. Finally, dienol **62** gave



62 **63**

evidence of accelerated [1,3]-benzyl shift, although this process was accompanied by rather extensive decomposition and dehydration.

Discussion and Summary

The first observation of an anionically accelerated [3,3]-sigmatropic rearrangement was made only 7 years ago.[4a] In the few intervening years the phenomenon has grown from this single example to become a general substituent effect observable in a variety of pericyclic reactions. However, information on the relative kinetic ranking of various pathways was not available at the onset of the present work. In the first phase of our study, oxyanionic substituent effects on [1,5]-hydrogen sigmatropy are shown to be of significantly lesser impact than those on [3,3]-carbon sigmatropy.

The perturbation produced by negatively charged oxygen on neighboring bond strengths has been previously estimated by thermochemical[3c] and theoretical means.[4c] Evans and Baillargeon considered the bond homolysis reaction $MOCH_2–R \rightarrow MOCH_2\cdot + \cdot R$ and concluded that radical stabilization is preferentially enhanced in the alkoxide anion as a consequence of electronic delocalization involving two-center, three-electron bonds. In the case wherein R = H, the change from M = H to M = K was estimated to facilitate the bond dissociation process by 17 kcal/mol, while for the R = CH_3 example, this was assessed to be 15 kcal/mol. The first conclusion agrees with that derived by Goddard from generalized valence-bond and configuration-interaction calculations, which show that flanking C–H bonds increase appreciably in length as the OM substituent becomes more ionic.[4c]

Although this ordering agrees qualitatively with our findings, the 2-kcal/mol gap is too small to account for the 10^4- to 10^5-fold slower [1,5]-hydrogen shifts. Alternative thinking in this laboratory is focused upon the greater bond strengths of $K^+{}^-OCH_2–H$ (76 kcal/mol) as compared to $K^+{}^-OCH_2–CH_3$ (68 kcal/mol), where the difference is substantially larger. If during the dissociation of these bonds a greater proportion of the initial ground-state energy terms is carried into the activated complex for bond dissociation, the large kinetic differences are better reconciled. This topic is certain to be the subject of additional analysis as additional studies are completed and more sophisticated theoretical parameters are introduced.

In another context, the chemical reactivity of trienols **29** and methyl ether **38** as summarized in Table V is most revealing. The data establish that the *extent* of rearrangement via the oxy-Cope pathway *increases* in both **29a** and **29b** as the donor properties of the oxygen atom are *decreased* ($K^+ \rightarrow Na^+ \rightarrow H^+$) and the *rate* of isomerization *falls off* ($K^+ > Na^+ > H^+$). In this respect, these results contrast with all prior studies that have shown oxy-Cope rearrangements to be kinetically accelerated in proportion to the increased donor properties of the dienol oxygen.[4] The unprecedented behavior of **29** is believed to be of conformational origin, **27** being more favored when the alkoxide is naked and relatively small in size. The structural geometry inherent to **27** is apparently not as favorable to [3,3]-carbon sigmatropy as it is in **27′**. Accordingly, it may prove of value when the chemistry of dienols is explored in the future to examine not only the rearrangement pathway adopted by the neutral system but also that adopted by their sodium and potassium salts. Conversion to the alkoxides need not result uniquely in enhancement of the rate of [3,3]-carbon shift. Other reaction pathways *may* also become accelerated, and to a higher level. Furthermore, in such circumstances the Na^+ salt *may* exhibit chemistry different from that of the K^+ alkoxide. Both species warrant investigation.

Finally, the extraordinarily facile dehydration[34] experienced by 1-alkyl-*cis*,*cis*-2,4-cyclononatrienols **41** deserves further comment, particularly in view of their role as possible precursors to the helical anions **50**. The conversion of **41** to **50** under mild conditions and the subsequent ready cyclization to **51** are suggestive that low reaction enthalpies are involved. In the later instance, the driving force arises from the transformation of a π bond into a σ bond (−20 kcal/mol). Importantly, this favorable energy term is not offset by the increased ring strain within **51** and its somewhat decreased delocalization energy. The bicyclo[4.3.1]decatetraenyl anion has been previously generated and shown unquestionably to be a delocalized Hückeloid species.[35] Molecules with rigid-coiled frameworks such as **50**, whether neutral or charged, can be expected to exhibit unusual levels of chemical reactivity and merit detailed investigation.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60, Varian EM-360, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C NMR spectra were recorded with a Bruker WP-80 or HX-90 spectrometer. Mass spectra were

(34) Usually, the dehydration of alcohols with base is effected at elevated temperatures. For example, see: (a) Bamberger, E.; Lodter, W. *Chem. Ber.* **1890**, *23*, 197. (b) Strauss, F.; Lemmel, L. *Ibid.* **1913**, *46*, 232. (c) Sabetay, S. *Bull. Soc. Chim. Fr.* **1929**, *45*, 69. (d) Sabetay, S.; Mintsou, T. *Ibid.* **1929**, *45*, 892. (e) Kitchen, L. J. *J. Am. Chem. Soc.* **1951**, *73*, 2368. (f) Ohloff, G.; Schade, G. *Angew. Chem.* **1955**, *67*, 427. (g) Ohloff, G. *Chem. Ber.* **1957**, *90*, 1554. (h) Ohloff, G. *Liebigs Ann. Chem.* **1959**, *627*, 79.

(35) (a) Radlick, P.; Rosen, W. *J. Am. Chem. Soc.* **1966**, *88*, 3461; **1967**, *89*, 5308. (b) Grimme, W.; Kaufhold, M.; Dettmeier, Y.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 604. (c) Murata, I.; Nakasuji, K.; Morita, T. *Chem. Lett.* **1974**, 743. (d) Takahashi, K.; Takase, K.; Kagawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 1186; *J. Chem. Soc., Chem. Commun.* **1979**, 863.

measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative-scale VPC separations were performed on Varian Aerograph Model A-90-P3 instruments equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2,4-Cycloheptadienol (6). 2,4-Cycloheptadienone[16,17] (2.1 g, 0.0194 mol) was placed in 20 mL of anhydrous ether and cooled to −78 °C under a nitrogen atmosphere. Diisobutylaluminum hydride (30 mL of 1.18 M in ether, 0.035 mol) was introduced via syringe over a 15-min period. The mixture was stirred at −78 °C for 1 h and at room temperature for another 1 h. Excess hydride was destroyed by addition of 10% sodium hydroxide solution until the evolution of hydrogen stopped. The reaction mixture was taken into a separatory funnel along with 100 mL of ether, where it was washed with water and brine before being dried. Solvent removal followed by distillation (with minimal heat application) delivered 2.0 g (94%) of 2,4-cycloheptadienol, bp 55–50 °C (0.1 mm). An analytical sample was prepared by VPC purification of a 2 ft × 0.25 in. 15% SF-96 column at 85 °C: ^{1}H NMR (CCl_4) δ 6.0–5.6 (m, 4 H), 4.6–4.3 (m, 1 H), 3.0 (br s, 1 H), 2.45–1.6 (m, 4 H); IR (neat, cm^{-1}) 3320, 3010, 2920, 2860, 1640, 1420, 1250, 1030, 850, 800; MS, *m/e* calcd (M^+) 110.0731, obsd 110.0734. Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.00; H, 9.15.

2,4-Cycloheptadienol-*1*-*d* (8). A solution of 2,4-cycloheptadienone (2.16 g, 0.02 mol) and cerous chloride (5.93 g, 0.02 mol) in methanol (50 mL) was cooled under a nitrogen atmosphere in an ice–water bath. Sodium borodeuteride (840 mg, 0.02 mol) was added in small portions at a rate such that the temperature of the reaction mixture did not exceed 5 °C. Complete addition of reagent was followed by further stirring for 10 min and subsequent quenching with glacial acetic acid (2 mL). The reaction mixture was diluted with water (150 mL) and washed in turn with water, saturated sodium bicarbonate, water, and brine prior to drying and solvent evaporation. The residue was distilled with minimal heat (oil bath at 45–50 °C), bp 30 °C (0.2 mm), and 1 g (42%) of **8** was isolated: ^{1}H NMR ($CDCl_3$) δ 5.8–5.6 (m, 4 H), 1.9 (s, 1 H), 2.4–1.8 (m, 4 H); IR (neat, cm^{-1}) 3350, 3010, 2970, 2100, 1640, 1420, 1370, 1230, 1070, 1040, 990, 940, 910, 850, 730; ^{13}C NMR (ppm, $CDCl_3$) 135.94, 134.97, 125.07, 124.71, 33.86, 25.06 (carbon-bearing deuterium not observed); MS, *m/e* calcd (M^+) 111.0794, obsd 111.0797.

***cis,cis*-2,4-Cyclooctadienol (10).** The procedure reported by Horinaka[19b] was followed to obtain two products that were readily separated by high-pressure liquid chromatography on silica gel with ethyl acetate in petroleum ether (5:95) as eluent. The two components proved to be **10** and *cis,cis*-1,5-cyclooctadien-3-ol (**11**) in a 5:1 ratio.

10: ^{1}H NMR (CCl_4) δ 5.8–5.2 (m, 4 H), 4.4–4.0 (m, 1 H), 4.0 (br s, 1 H), 2.2–1.2 (m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 135.36, 132.28, 125.21, 123.89, 69.98, 32.62, 28.31, 21.43.

11: ^{1}H NMr (CCl_4) δ 6.0–5.3 (m, 4 H), 4.0–3.6 (m, 1 H), 3.4 (br s, 1 H), 2.6–1.6 (m, 4 H).

***cis,cis*-2,4-Cyclononadienol (16). A. Singlet Oxygenation Route.** In a Pyrex photolysis vessel were placed *cis,cis*-1,4-cyclononadiene (12 g, 0.1 mol), rose bengal (600 mg), and methanol (300 mL), and the mixture was irradiated with a tungsten–halogen lamp for 30 h while oxygen was bubbled through the solution. The pink methanolic solution was mixed with cold water (300 mL), and sodium sulfite (20 g) was added. The resultant slurry was stirred for 2 h in an ice–water bath. Filtration of the solids followed by concentration of the filtrate under reduced pressure gave 100 mL of aqueous solution, which was extracted with ether (3 × 150 mL). The combined ether extracts were washed with water and brine before drying. Solvent was removed, and the residue was distilled to yield 6.5 g (48%) of a 1:1 mixture of **15** and **16**. The two products were separated by high-pressure liquid chromatography on silica gel, using 2% ethyl acetate–petroleum ether for elution. Final purification was achieved by distillation, bp 50 °C (0.1 mm).

16: ^{1}H NMR (CCl_4) δ 6.0–5.3 (m, 4 H), 4.4–4.0 (m, 1 H), 2.2–1.2 (m, 8 H), 1.6 (s, 1 H); IR (neat, cm^{-1}) 3300, 3000, 2920, 2830, 1620, 1450, 1080, 1020, 1000, 950, 760, 740; ^{13}C NMR (ppm, $CDCl_3$) 136.83, 134.08, 127.54, 126.87, 71.97, 36.13, 29.30, 26.27, 25.60; MS, *m/e* calcd (M^+) 138.1045, obsd 138.1048. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.88; H, 10.24.

15: ^{1}H NMR ($CDCl_3$) δ 5.8–5.1 (m, 4 H), 4.4–4.04 (m, 1 H), 2.7–1.3 (m, 8 H), 1.8 (s, 1 H); IR (neat, cm^{-1}) 3300, 3010, 2910, 2820, 1650, 1450, 1250, 1150, 1080, 1020, 880, 790, 730; ^{13}C NMR (ppm, $CDCl_3$) 136.48, 131.69, 127.50, 126.41, 70.03, 37.99, 27.43, 25.31, 24.34. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.80; H, 10.15.

B. Epoxidation Approach. A solution of *cis,cis*-1,4-cyclononadiene (2.6 g, 21.3 mmol) in 75 mL of methylene chloride was stirred mechanically at 0 °C while *m*-chloroperbenzoic acid (3.87 g, 21.3 mmol) was added over a 15-min period. The solution was stirred at 0 °C for an additional 6 h and washed with 10% sodium bicarbonate solution (2 × 50 mL) and brine (50 mL) prior to drying and removal of solvent. The crude epoxide (2.5 g, 85%) was of sufficient purity for use in subsequent reactions. An analytical sample of **17** was prepared by VPC purification on a 6 ft × 0.25 in. 5% SE-30 column: IR (film, cm^{-1}) 3010, 2980, 2920, 2860, 1640, 1000, 690; ^{1}H NMR ($CDCl_3$) δ 5.7–5.4 (m, 2 H), 3.2–2.8 (m, 2 H), 2.7–1.8 (series of m, 6 H), 1.8–1.2 (m, 4 H); MS, *m/e* calcd (M^+) 138.1045, obsd 138.1041. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.96; H, 10.19.

Lithium diisopropylamide solution was prepared from 100 mL of 1.1 N butyllithium (0.11 mol) in hexane and 15 mL of diisopropylamine (0.11 mol) in 200 mL of dry diethyl ether. The solution was stirred mechanically and cooled to 0 °C under a nitrogen atmosphere, while epoxide **17** (13 g, 0.094 mol) in 30 mL of ether was added from a pressure-equalizing dropping funnel during a 0.5-h period. Stirring was continued at 0 °C for an additional 6 h after which 100 mL of 10% ammonium chloride solution was added. The ethereal layer was separated and washed with 10% ammonium chloride solution and brine (50 mL) before drying. Solvent evaporation gave a yellow oil that consisted of alcohols **16** and **18** in an approximate 60:40 ratio. Final purification was achieved by HPLC on silica gel (8% ethyl acetate in petroleum ether). The spectra of **16** (6.5 g, 50%) proved identical with those of the dienol prepared above.

18: 5.2 g (40%); IR (film, cm^{-1}) 3350, 3010, 2940, 2860, 1645, 1445, 1050, 900, 725, 675; ^{1}H NMR ($CDCl_3$) δ 5.4 (br s, 2 H), 4.1–3.9 (m, 1 H), 2.6 (m, 1 H), 2.4–1.8 (m, 3 H), 1.8–1.4 (m, 6 H); MS, *m/e* calcd (M^+) 138.1044, obsd 138.1049.

***cis*-Bicyclo[4.3.0]non-4-en-2-one (19).** A solution of **18** (0.50 g, 3.6 mmol) in 15 mL of dry dichloromethane was stirred magnetically at ambient temperature while pyridinium chlorochromate (1.5 g, 7.2 mmol) was added as a solid over a 10-min period. After being stirred for an additional 5 h at room temperature, the solution was poured into 50 mL of diethyl ether and washed with saturated ammonium chloride solution and brine prior to drying. Removal of solvent afforded 0.45 g (90%) of a dark oil that was purified by column chromatography on silica gel (10% ethyl acetate–petroleum ether eluent) to give **19** as an oil: IR (neat, cm^{-1}) 3020, 2950, 2860, 1710, 1300, 1215, 1120, 955, 930, 890, 680; ^{1}H NMR ($CDCl_3$) δ 5.7 (m, 2 H), 3.2–2.6 (m, 4 H), 2.3–1.3 (m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 211.1, 130.8, 122.2, 51.5, 44.5, 37.9, 33.3, 27.2, 24.1; MS, *m/e* calcd (M^+) 136.0888, obsd 136.0890.

***cis*-Bicyclo[4.3.0]non-3-en-2-one (20).** A solution of 0.1 g (0.7 mmol) of **19** and *p*-toluenesulfonic acid (10 mg) in 10 mL of absolute ethanol was stirred at the reflux temperature for 24 h. Removal of solvent and purification by preparative TLC on silica gel (10% ethyl acetate in petroleum ether) gave 0.06 g (60%) of the α,β-unsaturated ketone: IR (film, cm^{-1}) 3020, 2960, 2880, 1665, 1380, 1250, 1220, 1200, 1120, 885, 810, 700; ^{1}H NMR ($CDCl_3$) δ 6.9–6.6 (m, 1 H), 5.9 (br d, J = 9 Hz, 1 H), 2.8–2.3 (m, 4 H), 2.3–1.4 (m, 6 H); MS, *m/e* calcd (M^+) 136.0888, obsd 136.0892.

Thermal Rearrangement of 6. 3-Cycloheptenone. Samples of **6** (30 mg) dissolved in benzene-d_6 (0.5 mL) were heated in sealed NMR tubes at 190 °C for 1 h or at 130 °C for 4 h to achieve complete disappearance of starting material. The sole product (VPC analysis) was identified as the β,γ-unsaturated ketone:[22] IR (neat, cm^{-1}) 1700; ^{1}H NMR (CCl_4) δ 6.0–5.5 (m, 2 H), 3.1–3.0 (m, 2 H), 2.4–1.4 (series of m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 209.49 (s), 131.49 (s), 120.11 (d), 42.73 (t), 43.62 (t), 29.96 (t), 21.75 (t).

Thermal Rearrangement of 10. 3-Cyclooctenone. *cis,cis*-2,4-Cyclooctadienol (100 mg, 0.8 mmol) in dry tetrahydrofuran (1 mL) was sealed under vacuum (0.1 mm) and heated in a pyrolysis chamber at 190 °C for 1 h. The single β,γ-unsaturated ketone product was isolated by VPC purification (4 ft × 0.25 in. 10% bentone and 10% SF-96 column, 115 °C), 60 mg (60%): IR (neat, cm^{-1}) 3025, 2940, 1710, 1400; ^{1}H NMR (CCl_4) δ 5.8–5.6 (m, 2 H), 3.1–2.9 (m, 2 H), 2.5–1.5 (m, 8 H);[22] ^{13}C NMR (ppm, $CDCl_3$) 213.57, 131.64, 124.31, 44.28, 42.26, 27.34, 25.95, 24.81; MS, *m/e* calcd (M^+) 124.0888, obsd 124.0890.

Thermal Rearrangement of 16. *cis*-3-Cyclononenone. A solution of **16** (30 mg) in carbon tetrachloride (0.5 mL) was sealed in an NMR tube and heated at 190 °C for 1 h. NMR analysis indicated the complete disappearance of **16**. The product, identified as the β,γ-unsaturated ketone, was isolated by preparative VPC (2 ft × 0.25 in. 10% SE-30 at 70 °C): IR (neat, cm^{-1}) 3010, 2920, 2840, 1710, 1650, 1470, 1450, 1330, 1270, 1240, 1200, 1120, 1050, 1020, 800, 780, 750, 730; ^{1}H NMr (CCl_4) δ 5.82–5.3 (m, 3 H), 3.1–3.0 (m, 2 H), 2.5–1.3 (m, 10 H)[22] MS, *m/e* calcd (M^+) 138.1045, obsd 138.1045.

Thermal Rearrangement of 8. 3-Cycloheptenone-*5*-*d*. A solution of **8** (50 mg, 4.5 mmol) in carbon tetrachloride (1 mL) was sealed in an NMR tube under vacuum (0.1 mm) and heated in a pyrolysis chamber at 150 °C. The progress of the reaction was monitored by NMR, which showed that all starting material disappeared after 3.5 h. The 3-cycloheptenone-*5*-*d* was isolated by VPC purification (2 ft × 0.25 in. 10% SF-96 column, 110 °C) along with a small amount of 2-cyclo-

heptenone-*5-d*: IR (neat, cm^{-1}) 1710; ^1H NMR (CCl_4) δ 5.8–5.4 (m, 2 H), 3.1 (m, 2 H), 2.5–2.2 (m, 3 H), 2.2–1.7 (m, 2 H); MS, *m/e* calcd (M^+) 111.0794, obsd 111.0800.

The conjugated isomer exhibited the following ^1H NMR spectrum (CCl_4) δ 6.5–5.4 (m, 2 H), 2.5–2.0 (m, 4 H), 2.0–1.6 (m, 3 H).

Anionic Rearrangement of 6. A slurry of potassium hydride (500 mg, 5 mmol) was prepared in dry tetrahydrofuran (25 mL) under nitrogen, where it was maintained at −4.5 °C with the aid of a thermostated cold bath. 2,4-Cycloheptadienol (150 mg, 1.36 mmol) in tetrahydrofuran (2 mL) was added, and the mixture was stirred for 14 h at −4.5 °C. Aqueous ammonium chloride solution was introduced slowly to quench the excess potassium hydride, and the aqueous layer was extracted with ether (2 × 50 mL). The combined ether extracts were washed with water and brine prior to drying. Solvent removal followed by distillation yielded 135 mg (90%) of a mixture of 3-cycloheptenone and **7** in a 3:2 ratio (VPC analysis). Final purification was achieved on a 4 ft × 0.25 in. 10% SE-30 column at 70 °C. The spectral properties of the β,γ-unsaturated ketone were identical with those described above.

7: ^1H NMR (CCl_4) δ 6.0–5.5 (m, 4 H), 4.4–4.0 (m, 1 H), 2.7–2.38 (m, 4 H), 2.0 (br s, 1 H).

Anionic Rearrangement of 8. 3,5-Cycloheptadienol-*1-d*. A slurry of potassium hydride (100 mg, 1 mmol) was prepared in the predescribed manner and placed in a thermostatically controlled bath at 5 °C. 2,4-Cycloheptadienol-*1-d* (100 mg, 0.9 mmol) in dry tetrahydrofuran was added, and progress of the reaction was followed by VPC. Complete conversion to product was observed after ca. 2.5 h. The reaction mixture was quenched with aqueous ammonium chloride solution (5 mL) and worked up in the standard way. The product was purified by VPC (2 ft × 0.25 in. 10% SF-96 column, 110 °C), and 80 mg (80%) of 3,5-cycloheptadienol-*1-d* was collected: IR (neat, cm^{-1}) 3300, 3010, 2920, 2820, 2100, 1610, 1440, 1420, 1350, 1230, 1070, 920, 850, 785, 665; ^1H NMR ($CDCl_3$) δ 6.0–5.6 (m, 4 H), 2.6–2.4 (m, 4 H), 1.9 (s, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 129.33, 127.59, 38.25 (carbon bearing the deuterium atom was not detected); MS, *m/e* calcd (M^+) 111.0794, obsd 111.0797.

Anionic Rearrangement of 10. A slurry of potassium hydride (200 mg, 2 mmol) in tetrahydrofuran (15 mL) was prepared according to previously described guidelines at 0 °C. A solution of *cis,cis*-2,4-cyclooctadienol (200 mg, 1.6 mmol) in tetrahydrofuran (1 mL) was added, and the mixture was stirred for 6 h at 0 °C. Quenching followed by molecular distillation gave 170 mg (85%) of 3-cyclooctenone.

Anionic Rearrangement of 16. A slurry of potassium hydride (2 g, 20 mmol) was prepared by the standard procedure in dry tetrahydrofuran (70 mL) and cooled to 0 °C. A solution of *cis,cis*-2,4-cyclononadienol (1.0 g, 7.25 mmol) in tetrahydrofuran (5 mL) was added, and the mixture was blanketed under a nitrogen atmosphere while being stirred at room temperature (24 °C). The progress of the reaction was monitored by VPC, and all starting material was consumed in 12 h. After the addition of aqueous ammonium chloride solution (25 mL), the predescribed workup was followed, and the product was purified by molecular distillation, which yielded 600 mg (60%) of *cis*-3-cyclononenone.

General Procedures for Kinetic Measurements. A. Thermal. A stock solution containing dienol (2 mg/mL) and internal standard (1 mg/mL) in dry tetrahydrofuran was prepared. Portions of the above solution (0.2 mL in size) were sealed in glass tubes under reduced pressure and immersed in an oil bath whose temperature was maintained within ±1 °C. These tubes were withdrawn from the bath at specified intervals and cooled in an ice–water bath. Samples of 1–2 μL were used for VPC analysis.

B. Anionic-Promoted Reactions. Potassium hydride (40% in oil, 200 mg, 2 mmol) was placed under a nitrogen atmosphere in a 100-mL round-bottomed flask equipped with a mechanical stirrer and washed with anhydrous ether (3 × 10 mL). Dry tetrahydrofuran (10–12 mL) was added to the above flask, which was immersed in a constant temperature bath. The mixture was stirred rapidly, and after about 15 min, a solution of dienol (30–40 mg) and internal standard (ca. 10 mg) in dry tetrahydrofuran (1 mL) was added, and a timer was started. Aliquots (0.5 mL) were withdrawn from the reaction vessel at specified intervals, quenched in vials containing saturated aqueous ammonium chloride solution (0.5 mL), and kept cold in an ice water bath. Samples 1–2 μL in size were taken from the organic layer and analyzed by VPC.

All VPC analyses were carried out on a Hewlett-Packard Model 5750 gas chromatograph equipped with a 6 ft × 0.125 in. 5% OV-225 column and flame ionization detector. Peak areas were determined by electronic integration. Retention times for the various products were verified by analyzing authentic samples. For **6** and **10**, the internal standard was diisopropylbenzene; *n*-heptadecane was utilized in the case of **16**.

***cis*-(2-Vinylcyclopentyl)acetaldehyde (24).** The standard procedure for anionic sigmatropy was followed starting with *cis,cis*-1,5-cyclononadien-3-ol (800 mg, 5.8 mmol). There was isolated 650 mg (81%) of product: IR (neat, cm^{-1}) 3060, 2950, 2880, 2700, 1730, 1640, 1450, 990, 900, 750; ^1H NMR ($CDCl_3$) δ 10.2 (m, 1 H), 6.0–4.76 (3m, 2 H), 2.9–1.3 (m, 10 H); MS, *m/e* calcd (M^+) 138.1045, obsd 138.1049.

***cis*-(2-Ethylcyclopentyl)acetic Acid (25).** A suspension of silver oxide was prepared by dissolving silver nitrate (5 g, 30 mmol) in water (40 mL) and adding sodium hydroxide (2.5 g, 60 mmol) in water (40 mL) with cooling. An ethanolic solution of aldehyde **24** (600 mg, 4.35 mmol) was added, and stirring was continued for 1 h at room temperature. The reaction mixture was acidified by addition of 20% hydrochloric acid (50 mL), and the solids were filtered. The filter cake was washed with hot 10% hydrochloric acid (2 × 20 mL), and the combined acidic portions were washed with ether (2 × 200 mL). The product was extracted from combined ether layers with 10% sodium hydroxide solution (2 × 50 mL). The basic solutions were acidified and extracted with ether (3 × 100 mL). The ether fractions were washed with water and brine before drying and solvent removal in vacuo to furnish 500 mg (82%) of the carboxylic acid. The material thus obtained was used without further purification.

A solution of this unsaturated acid in methanol (10 mL) along with palladium on carbon (50 mg) was hydrogenated under 50-psi pressure for 1 h at room temperature. Filtration followed by solvent removal afforded 530 mg (95%) of **25**: IR (neat, cm^{-1}) 2940, 2860, 2600, 1720, 1420, 1280, 1200, 980; ^1H NMR ($CDCl_3$) δ 10.7 (br s, 1 H), 2.5–0.8 (series of m, 15 H).

Methyl *cis*-(2-Ethylcyclopentyl)acetate (26). A sample of **25** was treated with excess diazomethane in ether, and the solution was allowed to stand at room temperature. VPC purification on a 12 ft × 0.25 in. 5% Carbowax 20M column (120 °C) gave the pure methyl ester: IR (neat, cm^{-1}) 2960, 2880, 1745, 1465, 1440, 1380, 1260, 1200, 1150, and 1020; ^1H NMR ($CDCl_3$) δ 3.6 (s, 3 H), 2.5–2.16 (m, 2 H), 2.1–1.1 (10 H), 1.1–0.9 (m, 3 H). These data were identical with those reported by Crouse.[24]

***cis,cis,cis*-2,4,7-Cyclononatrienone (28).** A solution of **1** (2.5 g, 18.4 mmol) in 40 mL of pentane was stirred mechanically while active manganese dioxide (16 g, 184 mmol) was added over a 2-h period. After an additional 24 h at room temperature, the solution was filtered and the solid was washed with 200 mL of ether. Concentration of the filtrate gave 1.55 g (65%) of the trienone as a clear oil, bp 48 °C (0.1 mm). HPLC on silica gel (10% ethyl acetate–petroleum ether) gave the analytical sample: IR (film, cm^{-1}) 3010, 2910, 2860, 1665, 1620, 1600, 1305, 1125, 790, 775, 728, 650; ^1H NMR ($CDCl_3$) δ 6.6–5.5 (series of m, 6 H), 3.35 (d, J = 6 Hz, 2 H), 2.8 (t, J = 6 Hz, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 200.4, 137.4, 136.6, 130.6, 130.2, 125.5, 124.7, 38.4, 27.1; UV λ_{max} (EtOH, 95%) 277 nm (ϵ 3400); MS, *m/e* calcd (M^+) 134.0732, obsd 134.0728. Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.26; H, 7.81.

A sample of this trienone was reduced with $LiAlH_4$ in dry diethyl ether at 0 °C. Usual workup afforded a single product, identical in all respects with an authentic sample of **1**.

1-Methyl-*cis,cis,cis*-2,4,7-cyclononatrien-1-ol (29a). To a solution of **28** (0.92 g, 6.8 mmol) dissolved in 20 mL of dry diethyl ether cooled to −78 °C was added 5 mL of 1.4 N methyllithium in hexane (7 mmol). The reaction mixture was allowed to warm slowly to 0 °C and poured into 20 mL of 10% aqueous ammonium chloride solution. The product was extracted into ether (50 mL), washed with brine, dried, and concentrated to give a light yellow oil. Medium-pressure liquid chromatography on silica gel (elution with 10% ethyl acetate–petroleum ether) gave 0.97 g (94%) of **29a** as a colorless oil: IR (film, cm^{-1}) 3400, 3010, 2960, 2920, 2860, 1650, 1450, 1095, 910, 865, 805, 770, 745; ^1H NMR ($CDCl_3$) δ 6.05–5.2 (m, 6 H), 2.95–2.3 (m, 5 H), 1.3 (s, 3 H); MS, *m/e* calcd (M^+) 150.1044, obsd 150.1040. Anal. Calcd for $C_{10}H_{14}O$: C, 80.01; H, 9.33. Found: C, 79.63; H, 9.43.

1-Ethyl-*cis,cis,cis*-2,4,7-cyclononatrien-1-ol (29b). Comparable treatment of **28** (1.55 g, 11.5 mmol) in cold (−78 °C), dry tetrahydrofuran (30 mL) with ethyllithium (20 mL of 1.0 M in ether, 20 mmol) gave a light yellow oil. Distillation (bp 48–52 °C) afforded pure **29b** as a colorless oil (1.5 g, 82%): IR (film, cm^{-1}) 3450, 3050, 2970, 2950, 1620, 1120, 970, 920, 795, 770, 695; ^1H NMR ($CDCl_3$) δ 6.1–5.7 (m, 6 H), 3.0–2.2 (m, 4 H), 1.6 (br q, $J \sim 7$ Hz, 2 H), 1.0 (t, J = 7 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 141.66, 129.38, 128.31, 127.34, 125.69, 123.26, 74.91, 36.94 (2C), 29.27, 8.01; UV λ_{max} (EtOH, 95%) 220 nm (sh, $\epsilon \sim 3000$); MS, *m/e* calcd (M^+) 164.1201, obsd 164.1205. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.62; H, 9.75.

Anionic Rearrangement of 29a (KH/18-Crown-6). Potassium hydride (0.35 g of 23.6% in oil, 2.0 mmol) was washed free of oil with ether and suspended in 10 mL of dry tetrahydrofuran. 18-Crown-6 (0.50 g, 1.9 mmol) was added, and the solution was cooled to −78 °C in a dry ice–acetone bath. A solution of trienol **29a** (0.25 g, 1.67 mmol) in 1 mL of tetrahydrofuran was added slowly, and the solution was warmed to −25 °C and stirred at that temperature for 2 h, at which point the reaction mixture was quenched by addition of excess 10% ammonium chloride

solution (10 mL). Standard workup followed by chromatography (MPLC, elution with 10% ethyl acetate–petroleum ether) gave trienol **30** (216 mg, 86%). Also isolated was 3 mg (<2%) of a mixture of dienones **36a** and **37a**.

30: mp 55–56 °C; IR (KBr, cm^{-1}) 3300, 3000, 2960, 2920, 1450, 1365, 1210, 1090, 990, 800, 765, 720, 650; ^1H NMR ($CDCl_3$) δ 6.0–5.2 (m, 6 H), 2.8 (t, J = 6 Hz, 2 H), 2.4 (dd, J = 8 and 1 Hz, 2 H), 1.8 (s, 1 H), 1.4 (s, 3 H); UV λ_{max} (EtOH, 95%) 235 nm (ϵ 5100); MS, m/e calcd (M^+) 150.1044, obsd 150.1038. Anal. Calcd for $C_{10}H_{14}O$: C, 80.01; H, 9.39. Found: C, 79.80; H, 9.33.

Catalytic Hydrogenation of 29a and 30. A. Starting with 29a. A mixture of **29a** (0.10 g, 0.67 mmol) and 10 mg of 5% palladium on carbon in 5 mL of ethyl acetate was hydrogenated at 50-psi pressure for 1 h. Filtration and evaporation of solvent gave 1-methylcyclononanol (90 mg, 90%) as a colorless oil: IR (film, cm^{-1}) 3400, 2940, 2880, 1490, 1375, 1100, 920; ^1H NMR ($CDCl_3$) δ 2.1 (br s, 1 H), 1.8–1.5 (m, 16 H), 1.15 (s, 3 H); MS, m/e calcd (M^+) 156.1514, obsd 156.1518.

B. Starting from 30. A mixture of trienol **30** (50 mg, 0.33 mmol) in 5 mL of ethyl acetate was hydrogenated for 1 h at 50-psi pressure over 10 mg of 5% palladium on carbon. Filtration and removal of solvent gave 1-methylcyclononanol, identical *in* all respects with the sample isolated above.

1-Methylene-*cis*,*cis*,*cis*-2,4,7-cyclononatriene (31). A. Wittig Olefination of 28. *n*-Butyllithium (1 mL of 1.6 N in hexane, 1.6 mmol) was added dropwise to a mechanically stirred slurry of methyltriphenylphosphonium bromide (0.55 g, 1.5 mmol) in 10 mL of dry ether at room temperature. After 15 min, a solution of **28** (0.20 g, 1.5 mmol) in 1 mL of ether was added via syringe. Stirring was continued for an additional 2 h. The solution was then filtered, concentrated, taken up in petroleum ether, and refiltered to remove precipitated triphenylphosphine oxide. Concentration gave a clear oil that was purified by VPC (12 ft × 0.25 in. 15% SE-30, 170 °C) to give **31** (123 mg, 65%): IR (film, cm^{-1}) 3100, 3020, 2930, 2860, 1645, 1490, 895, 795, 710, 650; ^1H NMR ($CDCl_3$) δ 6.35 (d, J = 12 Hz, 1 H), 6.0–5.2 (series of m, 5 H), 5.15 (s, 1 H), 4.75 (s, 1 H), 3.1 (d, J = 7 Hz, 2 H), 2.9 (t, J = 6 Hz, 2 H); MS, m/e calcd (M^+) 132.0939, obsd 132.0944. Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.74; H, 9.18.

B. Acid-Catalyzed Dehydration of 29a. A solution of **29a** (0.1 g, 0.67 mmol) and *p*-toluenesulfonic acid (5 mg) in 5 mL of benzene was stirred at room temperature for 48 h. Evaporation of solvent and MPLC purification on silica gel (100% petroleum ether as eluant) gave 65 mg (70%) of **31**, identical with the product isolated earlier. The remainder of the material proved to be a mixture of two or more alcohols and was not characterized.

3-Methyl-*cis*,*cis*,*cis*-cyclonona-2,5,7-trien-1-ol (32). A solution of trienol **30** (0.10 g, 0.67 mmol) in 5 ml of benzene was stirred at room temperature with a catalytic amount of *p*-toluenesulfonic acid. After 3 days the solvent was removed, and the residue was purified by MPLC by using 10% ethyl acetate in petroleum ether as eluant. The minor nonpolar fraction, possibly tetraene, was not characterized (15 mg). The major product, a colorless oil (65 mg, 65%), was identified as **32**: IR (film, cm^{-1}) 3400, 3020, 3000, 2960, 2860, 1640, 1335, 1060, 990, 910, 860, 800, 740; ^1H NMR ($CDCl_3$) δ 6.0–5.2 (m, 5 H), 4.4 (m, 1 H), 2.8 (dd, J = 12 and 8 Hz, 1 H), 2.6–2.3 (m, 3 H), 2.0 (br s, 1 H), 1.8 (s, 3 H); MS, m/e calcd (M^+) 150.1044, obsd 150.1038.

Pyridinium Chlorochromate Oxidation of 29a. A solution of **29a** (0.07 g, 0.47 mmol) in 10 mL of dry dichloromethane was stirred magnetically while pyridinium chlorochromate (0.17 g, 0.79 mmol) was added over a several-minute period. After 12 h the solution was poured into 50 mL of ether and washed with 10% saturated ammonium chloride solution (10 mL) and brine (10 mL). Drying and concentration gave a reddish oil that was purified by preparative TLC on silica gel. Elution with 10% ethyl acetate in petroleum ether gave 26 mg (38%) of 3-methyl-*cis*,-*cis*,*cis*-2,5,8-cyclononatrien-1-one (**35**) and 40 mg (57%) of 5-methyl-*cis*,*cis*,*cis*-2,4,7-cyclononatrien-1-one (**34**). Molecular distillation of **35** gave pure trienone: IR (film, cm^{-1}) 3050, 2970, 2930, 2850, 1640, 1610, 1000, 925, 855, 780, 750; UV λ_{max} (EtOH, 95%) 250 nm (ϵ 8900); ^1H NMR ($CDCl_3$) δ 6.3–5.6 (series of m, 5 H), 3.3–2.9 (m, 4 H), 1.88 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 194.0, 146.9, 133.0, 132.0, 130.5, 129.6, 127.2, 32.1, 26.8, 25.2; MS, m/e calcd (M^+) 148.0888, obsd 148.0886.

Molecular distillation of **34** gave analytically pure trienone: IR (film, cm^{-1}) 3030, 2960, 1665, 1635, 1605, 1050, 770; UV λ_{max} (EtOH, 95%) 286 nm (ϵ 5400); ^1H NMR ($CDCl_3$) δ 6.6–5.7 (series of m, 5 H), 3.3 (d, J = 6 Hz, 2 H), 2.8 (d, J = 6 Hz, 2 H), 1.88 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 220.3, 141.3, 138.2, 136.5, 122.1, 38.3, 32.0, 24.4; MS, m/e calcd (M^+) 148.0888, obsd 148.0884. Anal. Calcd for $C_{10}H_{12}O$: C, 81.05; H, 8.16. Found: C, 80.88; H, 8.25.

Pyridinium Chlorochromate Oxidation of 30. The preceding experimental conditions were employed for the oxidation of **30** (35.6 mg, 0.24 mmol) with 0.22 g (1 mmol) of pyridinium chlorochromate in 10 mL of dry dichloromethane. Preparative TLC on silica gel (10% ethyl acetate in petroleum ether) gave 28 mg (80%) of trienone **33** as an oil. Molecular distillation gave pure trienone: IR (film, cm^{-1}) 3010, 2960, 2930, 1680, 1650, 1460, 1425, 1150, 1290, 910, 810, 760, 700, 690; UV λ_{max} (EtOH, 95%) 227 nm (ϵ 7100), 250 sh (ϵ 5400); ^1H NMR ($CDCl_3$) δ 6.05–5.6 (m, 5 H), 3.2 (d, J = 8 Hz, 2 H), 2.85 (d, J = 6 Hz, 2 H), 1.88 (s, 3 H); MS, m/e calcd (M^+) 148.0888, obsd 148.0886.

Manganese Dioxide Oxidation of 32. A solution of **32** (0.027 g, 0.18 mmol) in 5 mL of dry benzene was stirred at room temperature with 0.20 g (2.3 mmol) of active manganese dioxide. After 12 h the solution was filtered through Celite and concentrated. The residue was homogeneous by TLC and displayed a ^1H NMR spectrum identical with that of trienone **33**.

Thermal Rearrangement of 29a. A base-washed glass ampule was charged with 100 mg (0.67 mmol) of **29a** and 250 mg of benzene-d_6. The solution was degassed, sealed in vacuo, and heated at 205 °C in a furnace for 2 h. The oily product was isolated by MPLC on silica gel (10% ethyl acetate–petroleum ether) and identified as ketone **36a** (0.86 g, 86%): IR (neat, cm^{-1}) 3050, 3000, 2930, 1718, 1640, 1155, 990, 910, 725; ^1H NMR ($CDCl_3$) δ 5.9–5.5 (m, 3 H), 5.05 (dd, J = 1 and 3 Hz, 1 H), 4.9 (t, J = 1 Hz, 1 H), 3.2–2.8 (m, 2 H), 2.6–2.2 (m, 4 H), 2.1 (s, 3 H); MS, m/e calcd (M^+) 150.1044, obsd 150.1040.

Anionic Rearrangement of 29a (KH Only). Potassium hydride (0.25 g of 23.6% in oil, 1.5 mmol) was washed free of oil with dry ether and stirred magnetically in dry tetrahydrofuran (10 mL) under nitrogen at 0 °C while **29a** (0.15 g, 1 mmol) dissolved in 1 mL of tetrahydrofuran was added slowly via syringe. After 3 h at 0 °C, the reaction mixture was poured into 20 mL of saturated ammonium chloride solution and worked up in the usual manner to afford, after medium-pressure liquid chromatography on silica gel (10% ethyl acetate–petroleum eluant), two fractions: trienol **30** (60 mg, 40%) and an inseparable mixture of double-bond isomers **36a** and **37a** (50 mg, 35%).

Anionic Rearrangement of 29a with Sodium Hydride. Sodium hydride (0.10 g of 50% in oil, 2 mmol) was washed free of oil with dry ether and suspended in dry tetrahydrofuran (10 mL) at room temperature while **29a** (0.2 g, 1.3 mmol) dissolved in 1 mL of tetrahydrofuran was added via syringe. The reaction mixture was stirred at reflux for 3 h, cooled, and poured into 20 mL of saturated ammonium chloride solution. Extraction into ether followed by the usual workup afforded a yellow oil that was subjected to medium-pressure chromatography on silica gel. Elution with 10% ethyl acetate–petroleum ether gave two fractions; the first consisted of double-bond isomers **36a** and **37a** (90% of the product mixture), and the second (10%) was identified as trienol **30**.

Anionic Rearrangement of 29a with Dimsyl Anion. A solution of **29a** (0.1 g, 0.67 mmol) in 10 mL of tetrahydrofuran was stirred magnetically under nitrogen at 0 °C while a solution of dimsylsodium (1 M in dimethyl sulfoxide; 1 mL, 1 mmol) was added via syringe. After 80 min at 0 °C the reaction was quenched by the addition of excess 10% ammonium chloride solution and the solution worked up in the usual manner to afford 0.93 g (93%) of essentially pure **30**.

Thermal Rearrangement of 30. A base-washed glass ampule was charged with 100 mg (0.67 mmol) of **30** and 250 mg of benzene-d_6. The solution was degassed, sealed in vacuo, and heated at 205 °C for 3 h. The oily product was isolated by MPLC on silica gel (10% ethyl acetate–petroleum ether) and identified as ketone **37a** (0.85 g, 85%): IR (neat, cm^{-1}) 3060, 2980, 2940, 2850, 1718, 1640, 1460, 1410, 1365, 1110, 1000, 910, 715; ^1H NMR ($CDCl_3$) δ 5.9–5.3 (series of m, 3 H), 5.0 (dd, J = 1 and 3 Hz, 1 H), 4.90 (t, J = 3 Hz, 1 H), 3.3 (t, J = 8 Hz, 1 H), 3.2–2.2 (series of m, 5 H), 2.1 (s, 3 H).

The tosylhydrazone was obtained as a colorless crystalline solid, mp 125–127 °C: MS, m/e calcd (M^+) 318.1402, obsd 318.1393. Anal. Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.17; H, 6.91. Found: C, 63.85; H, 7.05.

Anionic Rearrangement of 29b (KH only). An oil-free suspension of potassium hydride (from 1.3 g of 23.6% in oil, 6.5 mmol) in dry tetrahydrofuran (10 mL) was stirred under nitrogen at 0 °C while **29b** (0.70 g, 4.9 mmol) was injected via syringe. After 3.5 h at 0 °C, the reaction mixture was poured into 25 mL of saturated ammonium chloride solution and extracted with two 50-mL portions of diethyl ether. The combined organic layers were washed with brine, dried, and concentrated. The light yellow residual oil was separated into three components by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). The first fraction contained double-bond isomers **36b** and **37b**, which were inseparable (0.14 g, 20%): IR (film, cm^{-1}) 3060, 2980, 2940, 2840, 1720, 1635, 1110, 1000, 910, 770, 710; ^1H NMR ($CDCl_3$) δ 6.0–5.4 (m, 2 H), 5.05 (dd, J = 3 and 1 Hz, 1 H), 4.9 (t, J = 1 Hz, 1 H), 3.4–2.0 (series of m, 8 H), 1.05 (t, J = 7 Hz, 3 H); MS, m/e calcd (M^+) 164.1201, obsd 164.1205. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.14; H, 9.83.

The second fraction was a dienone of unknown composition (23 mg, 4%).

The third fraction was identified as 1-ethyl-*cis,cis,cis*-2,5,7-cyclononatrien-1-ol (0.41 g, 55%): IR (film, cm^{-1}) 3400, 3020, 2960, 2920, 1650, 1630, 1215, 990, 945, 720, 655; ^1H NMR ($CDCl_3$) δ 6.0–5.2 (m, 6 H), 2.9 (m, 2 H), 2.6 (dd, J = 8 and 5 Hz, 2 H), 1.7 (distorted q, J = 7 Hz, 2 H), 1.05 (t, J = 7 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 138.0, 128.2, 127.8, 127.0, 125.0, 123.0, 77.6, 41.8, 36.6, 29.2, 7.9; MS, m/e calcd (M^+) 164.1201, obsd 164.1205. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.62; H, 9.83.

1-(*cis*-4-Vinyl-3-cyclopentenyl)-2-butanone (37b). A solution of 1-ethyl-*cis,cis,cis*-2,4,7-cyclononatrien-1-ol (0.10 g, 0.67 mmol) in toluene-d_6 (250 mg) was degassed and sealed in vacuo inside a thick-walled NMR tube. After being heated for 2 h at 210 °C, the tube was cooled, and the contents were removed and concentrated. Filtration of the yellow oil through silica gel (ether eluant) gave pure dienone **37b** as a colorless oil: IR (film, cm^{-1}) 3030, 2960, 2920, 1715, 1670, 1645, 1455, 1420, 775, 760; ^1H NMR ($CDCl_3$) δ 5.9–5.4 (m, 3 H), 5.0 (m, 1 H), 4.9 (m, 1 H), 3.3–2.75 (m, 3 H), 2.6–2.1 (m, 5 H), 1.05 (t, J = 7 Hz, 3 H); MS, m/e calcd (M^+) 164.1201, obsd 164.1205.

1-(*cis*-3-Vinyl-4-cyclopentenyl)-2-butanone (36b). A solution of **29b** (0.10 g, 0.67 mmol) in toluene-d_8 (250 mg) was degassed, sealed, and heated as described above. After heating for 2 h at 210 °C, the solution was cooled and processed as above to yield 90 mg (90%) of pure **36b**: IR (film, cm^{-1}) 3060, 2960, 2850, 1715, 1410, 1360, 1160, 1000, 910, 750, 715; ^1H NMR ($CDCl_3$) δ 5.8–5.3 (m, 3 H), 5.0 (m, 1 H), 4.9 (m, 1 H), 3.3 (t, J = 7 Hz, 1 H), 3.0–2.6 (m, 1 H), 2.6–1.9 (m, 6 H), 1.05 (t, J = 7 Hz, 3 H); MS, m/e calcd (M^+) 164.1201, obsd 164.1205.

1-Methoxy-1-methyl-*cis,cis,cis*-2,4,7-cyclononatriene (38). Potassium hydride (0.5 g of 23.6% in oil, 2.9 mmol) was washed free of oil with ether (2 × 10 mL) and stirred at −20 °C in 10 mL of dry ether. 1-Methyl-*cis,cis,cis*-2,4,7-cyclononatrienol (**29a**, 0.26 g, 1.7 mmol) was added dropwise via syringe. After 30 min at −20 °C, methyl iodide (0.30 g, 2.1 mmol) was added, and the solution was allowed to warm to room temperature. After an additional 3 h, the reaction mixture was poured into 30 mL of 10% ammonium chloride solution, extracted with diethyl ether (50 mL), washed with saturated brine, dried, and concentrated in vacuo to yield a light yellow oil. Purification by MPLC on silica gel (8% ethyl acetate–petroleum ether) gave 0.21 g (75%) of pure **38** as a colorless oil: IR (film, cm^{-1}) 3020, 2980, 2940, 2830, 1640, 1450, 1370, 1090, 810, 770; ^1H NMR ($CDCl_3$) δ 5.95–5.4 (series of m, 6 H), 3.25 (s, 3 H), 2.95–2.6 (m, 3 H), 2.5–2.3 (m, 1 H), 1.20 (s, 3 H); MS, m/e calcd (M^+) 164.1201, obsd 164.1205. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: 80.58; H, 9.87.

1-Methoxy-1-methyl-*cis,cis,cis*-2,5,7-cyclononatriene. The identical procedure was used for the conversion of 1-methyl-*cis,cis,cis*-2,5,7-cyclononatrien-1-ol (0.20 g, 1.2 mmol) to its methyl ether. Product purification by MPLC on silica gel (8% ethyl acetate–petroleum ether) afforded 0.074 g (76%) of colorless oily product: IR (film, cm^{-1}) 3020, 2980, 2940, 2820, 1630, 1450, 1100, 1070, 910, 785, 760, 740, 670; ^1H NMR ($CDCl_3$) δ 5.8–5.25 (series of m, 6 H), 3.2 (s, 3 H), 3.1 (t, J = 6 Hz, 1 H), 2.9–2.7 (m, 1 H), 2.7–2.2 (series of m, 2 H), 1.35 (s, 3 H); MS, m/e calcd (M^+) 164.1201, obsd 164.1204. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.80. Found: C, 80.45; H, 9.82.

Anionic Rearrangement of 38. A. Potassium Ethoxide. Potassium ethoxide was prepared from 30 mg (0.65 mmol) of ethanol and 0.20 g of potassium hydride (23.6% oil dispersion, 1.2 mmol) in 10 mL of anhydrous diethyl ether. Methoxy triene **38** (0.068 g, 0.4 mmol) dissolved in 1 mL of ether was added, and the solution was stirred under nitrogen at room temperature for 3 h. The usual workup afforded a clear oil that was subjected to immediate NMR analysis. Two tertiary methyl singlets were observed in a 10:1 integrated ratio at δ 1.20 and 1.35, respectively, corresponding to approximately 10% conversion to 2,5,7-cyclononatriene.

B. Potassium Ethoxide and 18-Crown-6. Potassium ethoxide was prepared from 0.014 (0.3 mmol) of absolute ethanol and 0.10 g (0.6 mmol) of potassium hydride (23.6% oil dispersion, washed free of oil with ether) in 10 mL of dry ether. Methoxy triene **38** (0.05 g, 0.3 mmol) and 18-crown-6 (0.08 g, 0.3 mmol) were added to the cooled (−20 °C) stirred solution, and the reaction was allowed to proceed at −20 °C for 2 h. The usual workup afforded a yellow oil, the ^1H NMR spectrum of which showed methyl singlets at δ 1.2 and 1.35 in a 1:9 integrated ratio, representing approximately 90% conversion to 2,5,7-cyclononatriene.

***cis,cis*-2,4-Cyclononadienone (39).** A solution of **10** (0.16 g, 1.1 mmol) in 10 mL of dichloromethane was stirred at room temperature while pyridinium chlorochromate (0.75 g, 3.5 mmol) was added as a solid over a 15-min period. After 5 h, the black tarry reaction mixture was poured into 50 mL of diethyl ether and shaken. The supernatant liquid was decanted from the tarry residue, washed with 50 mL of 10% ammonium chloride solution and 50 mL of brine, dried, and concentrated. The dark oil was filtered through silica gel (ether elution) to give **39** of >95% purity (0.14 g, 90%). MPLC purification on silica gel (10% ethyl acetate–petroleum ether) gave pure **39** as a colorless oil: IR (film, cm^{-1}) 3010, 2860, 1660, 1610, 1130, 1080, 995, 830, 810, 755, 660; ^1H NMR ($CDCl_3$) δ 6.5–5.8 (m, 4 H), 2.6–2.4 (m, 2 H), 2.1–1.5 (m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 206.0, 140.6, 135.6, 133.0, 123.0, 36.05, 26.8, 23.6, 22.4; MS, m/e calcd (M^+) 136.0884, obsd 136.0888. Anal. Calcd for $C_9H_{12}O$: C, 79.42; H, 8.83. Found: C, 79.38; H, 8.90.

1-Methylene-*cis,cis*-2,4-cyclononadiene (40). Methyllithium in hexane (1.4 N, 2.5 mL, 3.1 mmol) was added dropwise to a magnetically stirred solution of methyltriphenylphosphonium bromide (1.10 g, 3.1 mmol) in 15 mL of dry ether at room temperature. After an additional 15 min, **39** (0.40 g, 2.9 mmol) dissolved in 1 mL of dry ether was added dropwise via syringe. After 2 h the reaction mixture was filtered, concentrated, taken up in petroleum ether, and refiltered to remove precipitated triphenylphosphine oxide. Concentration gave a clear oil (0.33 g, 83%) that could be purified further by gas chromatography (6 ft × 0.25 in. 5% SE-30, 160 °C): colorless oil; IR (film, cm^{-1}) 3080, 3010, 2940, 2870, 1620, 1590, 1455, 880, 790, 750; ^1H NMR ($CDCl_3$) δ 6.2–5.4 (series of m, 4 H), 5.95 (d, J = 2.5 Hz, 2 H), 2.5–2.3 (m, 2 H), 2.1 (m, 2 H), 1.9–1.5 (m, 4 H); MS, m/e calcd (M^+) 134.1095, obsd 134.1099. Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.41; H, 10.47.

1-Methyl-*cis,cis*-2,4-cyclononadien-1-ol (41a). To a magnetically stirred solution of **39** (0.23 g, 1.7 mmol) in dry diethyl ether (10 mL) cooled to −78 °C was added methyllithium (1.4 N in ether, 2 mL, 2.8 mmol) via syringe through a rubber septum. The solution was allowed to warm to 0 °C during 1 h and then the reaction was quenched by the addition of excess 10% ammonium chloride solution (10 mL). The product was extracted into ether (2 × 50 mL), and the combined organic layers were washed prior to drying and evaporation of solvent. Column chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) gave 0.10 g (75%) of **41a** as a colorless oil: IR (film, cm^{-1}) 3400, 3005, 2960, 2930, 2850, 1630, 1110, 900, 810, 800, 730, 720, 650; ^1H NMR ($CDCl_3$) δ 5.9–5.4 (m, 4 H), 2.3–1.3 (m, 9 H), 1.2 (s, 3 H); MS, m/e calcd (M^+) 152.1201, obsd 152.1197. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.87; H, 10.61.

The following analogues were prepared in entirely comparable fashion.

1-(Methyl-d_3)-*cis,cis*-2,4-cyclononadien-1-ol (41b): 77% yield; IR (film, cm^{-1}) 3400, 3005, 2940, 2860, 2220, 1450, 1085, 1040, 960, 810, 725, 710; ^1H NMR ($CDCl_3$) δ 5.9–5.5 (m, 4 H), 2.3–2.0 (m, 3 H), 1.8 (s, 1 H), 1.8–1.3 (m, 5 H); MS, m/e calcd (M^+) 155.1389, obsd 155.1393.

1-Ethyl-*cis,cis*-2,4-cyclononadien-1-ol (41c): 82% yield; IR (film, cm^{-1}) 3400, 1690, 1640, 1450, 1100, 945, 730, 715; ^1H NMR ($CDCl_3$) δ 5.95–5.4 (m, 4 H), 2.3–1.0 (m, 4 H), 1.9–1.3 (m, 8 H), 0.9 (t, J = 8 Hz, 3 H); MS, m/e calcd (M^+) 166.1353, obsd 166.1357.

1-Isopropyl-*cis,cis*-2,4-cyclononadien-1-ol (41d). The isopropyl Grignard reagent was prepared from 0.10 g (4 mmol) of magnesium turnings and 0.25 g (2 mmol) of isopropyl bromide in 20 mL of dry diethyl ether. The solution was stirred and cooled to 0 C under a nitrogen atmosphere while **39** (0.20 g, 1.5 mmol) dissolved in 5 mL of dry diethyl ether was added via syringe through a rubber septum. Stirring was continued at 0 °C for an additional 15 min, at which point the reaction mixture was quenched by addition of excess 10% ammonium chloride solution (10 mL). Standard workup gave a light yellow oil that consisted of starting material, **41d**, and 1,4 addition product in a 1:5:4 ratio (MPLC integration). Final purification was achieved by MPLC on silica gel (10% ethyl acetate in petroleum ether), which gave 0.08 g (30%) of **41d**: IR (film, cm^{-1}) 3450, 2920, 2860, 1680, 1600, 1115, 1070, 1030, 990, 915, 790, 765, 710; ^1H NMR ($CDCl_3$) δ 6.0–5.4 (m, 4 H), 2.4–2.0 (m, 4 H), 2.0–1.5 (m, 7 H), 1.5–1.2 (m, 1 H), 1.05 (d, J = 8 Hz, 6 H); MS, m/e calcd (M^+) 180.1514, obsd 180.1507.

The following analogues were prepared in entirely analogous fashion.

1-Allyl-*cis,cis*-2,4-cyclononadien-1-ol (41e): 84% yield; IR (film, cm^{-1}) 3400, 3070, 3000, 2950, 2920, 1640, 1440, 990, 900, 810, 770, 740, 670; ^1H NMR ($CDCl_3$) δ 6.0–5.4 (m, 5 H), 5.1 (br s, 1 H), 5.0 (m, 1 H), 2.3–2.0 (m, 4 H), 2.0–1.4 (m, 7 H); MS, m/e calcd ($M^+ - H_2O$) 160.1252, obsd 160.1248.

1-Cyclopropyl-*cis,cis*-2,4-cyclononadien-1-ol (41f): 83% yield; IR (film, cm^{-1}) 3450, 3080, 3000, 2910, 2850, 1625, 1020, 950, 905, 860, 810, 765, 725, 710; ^1H NMR ($CDCl_3$) δ 6.0–5.3 (m, 4 H), 2.4–2.1 (m, 3 H), 2.0–1.2 (m, 6 H), 1.1–0.8 (m, 1 H), 0.3 (dd, J = 1.5 and 8 Hz, 4 H); MS, m/e calcd ($M^+ - H_2O$) 160.1251, obsd 160.1246.

1-Benzyl-*cis,cis*-2,4-cyclononadien-1-ol (41g): 54% yield; IR (film, cm^{-1}) 3450, 3060, 3020, 2990, 2850, 1630, 1600, 1480, 1080, 1010, 950, 810, 755, 725, 695, 655; ^1H NMR ($CDCl_3$) δ 7.22 (s, 5 H), 5.95–5.3 (m, 4 H), 2.7 (AB, J = 3 Hz, 2 H), 2.3–2.0 (m, 3 H), 1.9–1.3 (m, 6 H); MS, m/e calcd (M^+) 228.1514, obsd 228.1521.

Anionic Rearrangement of 41a (KH Only). Potassium hydride (23.6% suspension in oil, 0.25 g, 1.5 mmol) was washed free of oil with dry ether (2 × 10 mL) and stirred magnetically in 20 mL of dry tetrahydrofuran under nitrogen while **41a** (0.17 g, 1.1 mmol) was added slowly via syr-

inge. The reaction mixture was heated at reflux for 3 h, cooled, and poured into saturated brine (25 mL). The product was extracted into ether (2 × 50 mL), dried, and carefully concentrated to give a yellow oil. Gas chromatography purification (12 ft × 0.25 in. 15% SE-30, 150 °C) separated the two products. The first was characterized as diene **43a** (40% of the product mixture): IR (neat, cm^{-1}) 3010, 2940, 2900, 2860, 1610, 1450, 1120, 1080, 990, 855, 830, 725, 690; UV λ_{max} (EtOH, 95%) 255 nm (ϵ 9200); ^1H NMR ($CDCl_3$) δ 5.8 (br s, 4 H), 2.7 (br m, 2 H), 2.0–1.4 (m, 8 H); ^{13}C NMR (ppm, $CDCl_3$) 138.6 (d), 125.4 (d), 36.0 (d), 32.4 (2 C), 29.6 (t), 18.1 (t); MS, *m/e* calcd (M^+) 134.1095, obsd 134.1091.

An *N*-methyltriazolinedione adduct was formed from 30 mg (0.22 mmol) of **43a** and 25 mg (0.22 mmol) of *N*-methyltriazolinedione in 5 mL of ethyl acetate (24 h, 20 °C). Removal of solvent and recrystallization from 20% ethyl acetate in petroleum ether gave 27 mg (50%) of a monoadduct (**45a** or **46a**): mp 126–127 °C; ^1H NMR ($CDCl_3$) δ 6.3 (dd, J = 6 and 4 Hz, 2 H), 4.0 (m, 2 H), 3.05 (s, 3 H), 2.4 (m, 2 H), 2.4–1.3 (series of m, 8 H); MS, *m/e* calcd (M^+) 247.1321, obsd 247.1316. Anal. Calcd for $C_{13}N_{17}N_3O_2$: C, 63.14; H, 6.93. Found: C, 63.17, H, 6.99.

The second product was identified as **42a** (60% of the product mixture): IR (neat, cm^{-1}) 3020, 2940, 2880, 1620, 1450, 990, 725, 690; ^1H NMR ($CDCl_3$) δ 5.75–5.6 (m, 3 H), 5.5–5.3 (m, 1 H), 2.3–1.9 (m, 2 H), 1.8–1.3 (m, 5 H), 1.05 (s, 3 H); MS, *m/e* calcd (M^+) 134.1095, obsd 134.1091.

A sample of **42a** (0.052 g, 0.39 mmol) was treated with *N*-methyltriazolinedione (0.044 g, 0.39 mmol) in 5 mL of ethyl acetate. Removal of solvent and recrystallization from 20% ethyl acetate in petroleum ether gave 60 mg (63%) of **44a** as clear crystals: mp 104–106 °C; ^1H NMR ($CDCl_3$) δ 6.5–6.2 (m, 2 H), 4.7 (m, 1 H), 4.5 (dd, J = 5 and 2 Hz, 2 H), 3.0 (s, 3 H), 2.2–1.8 (m, 2 H), 1.8–1.0 (m, 8 H, includes methyl singlet at δ 1.29); irradiation of the olefinic signals caused collapse of the δ 4.7 multiplet to a doublet (J = 3 Hz) and of the δ 4.5 doublet of doublets to a singlet; MS, *m/e* calcd (M^+) 247.1321, obsd 247.1316. Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93. Found: C, 63.20; H, 6.90.

Anionic Rearrangement of 41a (KH/18-Crown-6). Potassium hydride (0.20 g of a 23.6% suspension in oil, 1.2 mmol) was washed free of oil with diethyl ether (2 × 10 mL) and stirred magnetically under nitrogen with 10 mL of dry diethyl ether. 18-Crown-6 (0.215 g, 0.82 mmol) and **41a** (0.115 g, 0.76 mmol) were added consecutively at ambient temperature, and the reaction mixture was stirred for an additional 2 h before being poured into cold brine (20 mL). The products were extracted into diethyl ether (50 mL), washed with brine, dried, and concentrated carefully in vacuo. GLC purification (15% SE-30) gave 0.034 g (34%) of a light oil identical in all respects with **43a** isolated earlier.

Catalytic Hydrogenation of 43a. A mixture of **43a** (0.015 g, 0.11 mmol) and 5% palladium on carbon (5 mg) in 5 mL of ethyl acetate was hydrogenated at 50-psi pressure for 1 h at room temperature. Filtration followed by solvent removal afforded 10 mg (66%) of bicyclo[4.3.1]decane: mp 80–83 °C; IR (film, cm^{-1}) 2860, 2820, 2780, 1440, 1360, 1220, 1080; ^1H NMR ($CDCl_3$) δ 2.0 (m, 2 H), 1.7–1.2 (m, 14 H); MS, *m/e* calcd (M^+) 138.1408, obsd 138.1413.

A sample of bicyclo[4.3.1]deca-2,4,6,8-tetraene (2 mg), kindly supplied by Professor Shechter, was hydrogenated in the same manner to deliver a saturated hydrocarbon, the NMR spectrum of which proved to be identical with that of the sample isolated above.

Anionic Rearrangement of 41c (KH only). From the reaction of 0.12 g (0.72 mmol) of **41c** with 1.4 mmol of oil-free potassium hydride in 20 mL of dry tetrahydrofuran at 66 °C for 2 h, there was obtained two major hydrocarbon products in a 71:27 ratio (VPC analysis). The minor fraction was identified as **43c** (R_1 = CH_3, R_2 = H): mp 48.5–50 °C; IR (neat, cm^{-1}) 3060, 3010, 2980, 2840, 1608, 1440, 1365, 1110, 990, 840, 800, 710, 680; ^1H NMR ($CDCl_3$) δ 6.0–5.5 (m, 4 H), 2.4 (br m, 2 H), 2.2–1.2 (series of m, 7 H), 0.8 (d, J = 7 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 135.5, 126.2, 42.5, 33.6, 33.5, 19.0, 17.0; MS, *m/e* calcd (M^+) 148.1252, obsd 148.1257. Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.12; H, 10.88.

The major fraction, a colorless oil, was identified as **42c** (R_1 = CH_3, R_2 = H): IR (neat, cm^{-1}) 3050, 3020, 2940, 2860, 1580, 1450, 1325, 940, 910, 780, 695; ^1H NMR ($CDCl_3$) δ 5.9–5.6 (m, 3 H), 5.5–5.3 (m, 1 H), 2.3–1.9 (m, 2 H), 1.8–1.2 (m, 7 H), 0.85 (t, J = 6 Hz, 3 H); MS, *m/e* calcd (M^+) 148.1252, obsd 148.1264.

A sample of **42c** (0.033 g, 0.2 mmol) was treated with *N*-methyltriazolinedione (0.025 g, 0.2 mmol) in 5 mL of ethyl acetate at room temperature. Removal of solvent and recrystallization from 15% ethyl acetate in petroleum ether gave 0.042 g (72%) of **44c** (R_1 = CH_3, R_2 = H) as clear needles: mp 124–125 °C; ^1H NMR ($CDCl_3$) δ 6.4–6.2 (m, 2 H), 5.8–5.6 (m, 2 H), 3.0 (s, 3 H), 2.2–1.2 (series of m, 9 H), 1.0 (t, J = 7 Hz, 3 H); MS, *m/e* calcd (M^+) 261.1477, obsd 261.1469. Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33. Found: C, 64.28; H, 7.42.

Anionic Rearrangement of 41c (KH/18-Crown-6). Treatment of **41c** (0.20 g, 1.2 mmol) with potassium hydride (0.25 g of 23.6% suspension, 1.5 mmol) and 18-crown-6 (0.34 g, 1.3 mmol) *in* 10 mL of diethyl ether under the predescribed conditions gave after 2 h a yellow oil that was homogeneous by GLC and TLC. VPC purification (15% SE-30) gave 0.113 g (64%) of **43c** as a waxy solid identical with the product isolated earlier.

Anionic Rearrangement of 41d (KH only). Treatment of **41d** (0.27 g, 0.94 mmol) with potassium hydride (0.25 g of 23.6% in oil, 1.5 mmol) in 20 mL of dry tetrahydrofuran under the predescribed conditions led after 4 h at 66 °C to the production of three isomeric hydrocarbons in a ratio (VPC analysis, 5% SE-30, 150 °C) of 75:15:10.

The earliest fraction **42d** (R_1 = R_2 = CH_3) was isolated as an oil: IR (neat, cm^{-1}) 3040, 2960, 2880, 1640, 1585, 1380, 1365, 990, 915, 850, 700; ^1H NMR ($CDCl_3$) δ 6.9–6.5 (m, 3 H), 5.3 (distorted d, $J \sim$ 10 Hz, 1 H), 2.4–2.1 (m, 1 H), 2.1–1.2 (series of m, 6 H), 1.2–1.0 (overlapping d, J = 7 Hz, 6 H); MS, *m/e* calcd (M^+) 162.1408, obsd 162.1412.

A portion of this diene sample (12 mg, 0.09 mmol) was reacted with *N*-methyltriazolinedione (10 mg, 0.09 mmol) in 5 mL of ethyl acetate at ambient temperature. Removal of solvent and recrystallization from 20% ethyl acetate gave 16 mg (77%) of **44d** (R_1 = R_2 = CH_3) as a crystalline solid: mp 159.5–160.5 °C; ^1H NMR ($CDCl_3$) δ 6.4–6.2 (m, 2 H), 4.8–4.6 (m, 2 H), 3.0 (s, 3 H), 2.4 (m, 1 H), 2.1–1.1 (series of m, 7 H), 1.0 (two d, J = 7 Hz, 6 H); MS, *m/e* calcd (M^+) 275.1634, obsd 275.1640. Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69. Found: C, 65.38; H, 7.71.

The second product, tentatively identified as 2-isopropyl-*cis*-bicyclo-[4.3.0]nona-2,4-diene, proved to be an oil: IR (neat, cm^{-1}) 3020, 2980, 2860, 1635, 1450, 910, 780, 690; ^1H NMR ($CDCl_3$) δ 5.8–5.6 (m, 1 H), 5.5 (d, J = 5 Hz, 1 H), 5.3 (dd, J = 8 and 3 Hz, 1 H), 2.9 (m, 1 H), 2.5–2.2 (m, 2 H), 2.2–1.3 (series of m, 6 H), 1.05 (d, J = 7 Hz, 6 H); MS, *m/e* calcd (M^+) 162.1408, obsd 162.1412.

A portion of this hydrocarbon (16 mg, 0.1 mmol) was reacted with *N*-methyltriazolinedione (11 mg, 0.1 mmol) in 5 mL of ethyl acetate. Evaporation of solvent and recrystallization from 20% ethyl acetate in petroleum ether gave a crystalline monoadduct; 24 mg (90%): mp 133 °C; ^{1} H NMR ($CDCl_3$) δ 6.3 (d, J = 3 Hz, 2 H), 4.8 (m, 1 H), 3.0 (s, 3 H), 2.7–2.4 (m, 2 H), 2.0–1.5 (m, 3 H), 1.5–1.0 (m including two d at δ 1.3 and 1.5, J = 7 Hz, total area = 9 H); MS, *m/e* calcd (M^+) 275.1634, obsd 275.1628.

The third hydrocarbon was identified as **43d** (R_1 = R_2 = CH_3): mp 94–96 °C; IR (KBr, cm^{-1}) 3020, 2980, 2920, 2860, 1640, 1610, 1450, 1100, 990, 800, 710, 680; ^1H NMR ($CDCl_3$) δ 6.0–5.5 (m, 4 H), 2.3–2.1 (m, 2 H), 2.1–1.7 (m, 2 H), 1.5–1.3 (m, 4 H), 1.20 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 135.64, 125.5, 46.6, 31.5, 28.2, 27.9, 27.7, 16.5; MS, *m/e* calcd (M^+) 162.1408, obsd 162.1412. Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.63; H, 11.16.

Anionic Rearrangement of 41d (KH/18-Crown-6). Treatment of **41d** (0.12 g, 0.67 mmol) with potassium hydride (0.25 g, 23.6% oil suspension, 1.5 mmol) and 18-crown-6 (0.25 g, 0.95 mmol) in 10 mL of diethyl ether under the predescribed conditions gave after 24 h at room temperature a yellow oil that consisted of the identical three compounds isolated earlier, in the corresponding ratio (VPC analysis) of 12:19:68, respectively.

Anionic Rearrangement of 41b (KH/18-Crown-6). Treatment of dienol **41b** (0.20 g, 1.3 mmol) with oil-free potassium hydride (0.30 g of 23.6% in oil, 1.8 mmol) and 18-crown-6 (0.45 g, 1.7 mmol) in 10 mL of dry diethyl ether led after 2 h at ambient temperature to the formation of a single hydrocarbon product (VPC analysis). The NMR was nearly identical with **43a**, and the mass spectrum gave evidence for mono- and dideuterated hydrocarbons: ^1H NMR ($CDCl_3$) δ 5.8 (br s, 4 H), 2.7 (br m, 2 H), 2.0–1.2 (series of m, <8 H); MS, *m/e* calcd (M^+) 136.1221, obsd 136.1216.

Anionic Rearrangement of 41f (KH only). Treatment of 0.115 g (0.63 mmol) of **41f** with 0.25 g (1.4 mmol) of potassium hydride (23.6% suspension in oil) in 20 mL of dry tetrahydrofuran under the predescribed conditions led after 3 h to the production of a single compound (**42f**) as a clear oil. Gas chromatographic purification (15% SE-30, 150 °C) gave 0.035 g (34%) of pure diene: IR (film, cm^{-1}) 3080, 3060, 3030, 3000, 2950, 2860, 1630, 1010, 905, 815, 695; ^1H NMR ($CDCl_3$) δ 5.9–5.6 (m, 3 H), 5.3–5.1 (m, 1 H), 2.5–2.3 (m, 1 H), 2.3–1.9 (m, 1 H), 1.7–1.3 (m, 5 H), 0.9–0.6 (m, 1 H), 0.4–0.2 (m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 132.3 (d), 130.6 (d), 131.12 (d), 120.15 (d), 44.8 (d), 43.9 (s), 39.3 (t), 35.8 (t), 22.6 (t), 20.5 (t), 0.63, –0.43 (m); MS, *m/e* calcd (M^+) 160.1252, obsd 160.1255.

A triazolinedione adduct was prepared from 0.05 g (0.3 mmol) of **42f** (0.3 mmol) of *N*-methyltriazolinedione in 5 mL of dry ethyl acetate. Evaporation of solvent and recrystallization from 20% ethyl acetate in petroleum ether gave 65 mg (75%) of the monoadduct **44f**: mp 110–111

°C; ^{1}H NMR ($CDCl_3$) δ 6.5–6.3 (m, 2 H), 5.8–5.5 (m, 2 H), 3.0 (s, 3 H), 2.1 (dt, J = 3 and 8 Hz, 1 H), 2.1–1.0 (series of m, 6 H), 0.5–0.1 (m, 5 H); MS, m/e calcd (M^+) 273.1477, obsd 273.1485. Anal. Calcd for $C_{15}H_{19}N_3O_2$: C, 65.92; H, 7.01. Found: C, 65.88; H, 7.07.

Anionic Rearrangement of 41f (KH/18-Crown-6). Treatment of **41f** (0.50 g, 2.8 mmol) with 0.57 g (3.3 mmol) of potassium hydride (23.6% suspension in oil) and 0.85 g (3.2 mmol) of 18-crown-6 in 15 mL of dry diethyl ether led after 4 h at room temperature to the production of a single compound, homogeneous by TLC and GLC. VPC purification (15% SE-30, 150 °C) gave 0.256 g (56%) of **42f** identical with that isolated previously.

Anionic Rearrangement of 41g (KH only). Treatment of 0.21 g (0.95 mmol) of **41g** with oil-free potassium hydride (0.25 g of 23.6% in oil, 1.5 mmol) in 20 mL of dry tetrahydrofuran under the predescribed conditions led after 4 h at the reflux temperature to the production of two compounds, separable by MPLC on silica gel (10% ethyl acetate–petroleum ether). The polar fraction was identified as enone **19** (30 mg, 24%), which had been isolated and characterized previously. The nonpolar fraction, isolated as an oil, was identified as diene **43g** (R_1 = Ph, R_2 = H) (80 mg, 41%): IR (film, cm^{-1}) 3080, 3060, 3020, 2930, 2850, 1600, 1495, 1440, 1110, 1030, 865, 755, 710, 690; ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 5.8 (br s, 4 H), 3.3–2.8 (m, 3 H), 2.0–1.65 (m, 3 H), 1.6–1.3 (m, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 144.7 (s), 136.1 (d), 127.6 (d), 126.9 (2C), 125.7 (d), 44.2 (d), 40.6 (d), 33.9 (t), 17.1 (t); MS, m/e calcd (M^+) 210.1408, obsd 210.1413. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.42; H, 8.62.

Anionic Rearrangement of 41g (KH/18-Crown-6). Treatment of **41g** (0.15 g, 0.66 mmol) with 0.25 g (1.5 mmol) of 18-crown-6 in 10 mL of ether under the predescribed conditions led after 18 h at room temperature to the formation of a single product, homogeneous by TLC and MPLC. MPLC purification on silica gel gave pure **43g** (99 mg, 71%), identical with that obtained earlier.

Anionic Rearrangement of 41e (KH/18-Crown-6). Potassium hydride (0.25 g, 23.6% in oil, 1.4 mmol) was washed free of oil and stirred at 0 °C in 10 mL of dry ether while **41e** (0.15 g, 0.8 mmol) and 18-crown-6 (0.30 g, 1.1 mmol) were added consecutively. After 4 h, the reaction mixture was processed in the usual manner and subjected to MPLC chromatography on silica gel (10% ethyl acetate in petroleum ether). Two bands were removed; the first (<10 mg) consisted of unidentified dehydration products, and the second (94 mg, 63%) was identified as 3-allyl-*cis*-4-cyclononenone (**47**): IR (film, cm^{-1}) 1710, 1640, 990, 810; ^{1}H NMR ($CDCl_3$) δ 6.0–5.5 (m, 1 H), 5.5–5.3 (m, 2 H), 5.2 (m, 1 H), 5.0 (m, 1 H), 3.0–2.7 (m, 1 H), 2.7–1.5 (series of m, 12 H); MS, m/e calcd (M^+) 178.1356, obsd 178.1352.

***trans,trans*-2,4-Hexadien-1-ol (59).** Lithium aluminum hydride (0.75 g, 0.02 mol) was suspended in 50 mL of dry ether at 0 °C while sorbaldehyde (1.9 g, 0.02 mol) in 10 mL of ether was added dropwise via syringe. After 3 h 10% ammonium sulfate solution (5 mL) was added, and the solution was filtered and concentrated. Distillation afforded pure **59** (1.8 g, 95%) as an oil: bp 89–91 °C (20 mm); IR (film, cm^{-1}) 3350, 3020, 2910, 2850, 1660, 1090, 980, 920; ^{1}H NMR ($CDCl_3$) δ 6.2–5.3 (series of m, 4 H), 4.05 (d, J = 6 Hz, 2 H), 3.3 (s, 1 H), 1.75 (d, J = 6 Hz, 3 H); MS, m/e calcd (M^+) 98.0779, obsd 98.0777.

***trans,trans*-1,5,7-Nonatrien-4-ol (57).** The allyl Grignard reagent was prepared from 15.1 g (0.125 mol) of allyl bromide and 9.1 g (0.38 mol) of magnesium in 100 mL of ether. Sorbaldehyde (10 g, 0.10 mol) in 20 mL of dry ether was added to the stirred, cooled (0 °C) solution. After an additional 0.5 h at 0 °C, the product mixture was poured into 200 mL of ice and water, and the product was extracted with ether. After being washed with brine and dried, the solution was concentrated and distilled to afford 7.4 g (52%) of **57**: bp 55–58 °C (1.5 mm); IR (neat, cm^{-1}) 3400, 1640, 980, 910; ^{1}H NMR ($CDCl_3$) δ 6.3–5.3 (m, 5 H), 5.2 (m, 1 H), 5.05 (m, 1 H), 4.3–4.1 (m, 1 H), 2.6–2.2 (m, 3 H), 1.8 (*d*, J = 6 Hz, 3 H); MS, m/e calcd (M^+) 138.1045, obsd 138.1041. Anal. Calcd for $C_9H_{14}O$: C, 78.27; H, 10.15. Found: C, 78.27; H, 10.19.

***trans,trans*-1-Phenyl-3,5-heptadien-2-ol (62).** The benzyl Grignard reagent was prepared in the usual manner from 2.6 g (15 mmol) of benzyl bromide and 0.72 g (30 mmol) of magnesium turnings in 50 mL of dry ether. Sorbaldehyde (1.2 g, 12.5 mmol) in 10 mL of ether was added dropwise to the cooled (0 °C) solution. After an additional 0.5 h, the reaction mixture was poured into 50 mL of 10% ammonium chloride solution and worked up in the usual manner to afford 3.5 g of crude dienol. Medium-pressure chromatography on silica gel gave 1.4 g (59%) of pure **62**: IR (film, cm^{-1}) 3400, 3020, 2920, 2840, 1600, 1500, 1450, 1100, 1025, 985, 740, 690; ^{1}H NMR ($CDCl_3$) δ 7.2 (br s, 5 H), 6.3–5.4 (series of m, 4 H), 4.3 (m, 1 H), 2.9 (br d, J = 6 Hz, 2 H), 1.7 (d, J = 6 Hz, 3 H), 1.5 (s, 1 H); MS, m/e calcd ($M^+ - H_2O$) 170.1072, obsd 170.1066.

***cis,trans*-2,4-Hexadien-1-ol (60).** Lithium aluminum hydride (0.75 g, 0.02 mol) was suspended in 50 mL of dry diethyl ether at 0 °C while methyl-*cis,trans*-2,4-hexadienoate[36] (1.5 g, 0.012 mol) in 2 mL of ether was added dropwise over a several minute period. After an additional 3 h, saturated ammonium sulfate solution (5 mL) was added, and the solution was filtered and concentrated. Distillation afforded pure **60** (1.2 g, 80%) as a colorelss oil: bp 90 °C (20 mm); IR (film, cm^{-1}) 3350, 3020, 2910, 2880, 1650, 1450, 1025, 990, 950, 815; ^{1}H NMR ($CDCl_3$) δ 6.5–5.25 (series of m, 4 H), 4.2 (d, J = 7 Hz, 2 H), 3.2 (s, 1 H), 1.75 (d, J = 7 Hz, 3 H); MS, m/e calcd (M^+) 98.0779, obsd 98.0781.

Anionic Rearrangement of 57. A suspension of oil-free potassium hydride (from 0.25 g of 23.6% in oil, 1.4 mmol) in 15 mL of anhydrous tetrahydrofuran was stirred under nitrogen at ambient temperature while **57** (0.15 g, 1.1 mmol) and 18-crown-6 (0.32 g, 1.2 mmol) were added consecutively. The reaction mixture was stirred at the reflux temperature for 18 h, cooled, and worked up in the usual manner to afford a dark volatile oil. The major component of this product mixture (0.071 g, 47%), which was isolated by medium-pressure chromatography on silica gel (5% ethyl acetate–petroleum ether eluant) proved to be **58**: IR (film, cm^{-1}) 3080, 3000, 2920, 2820, 1730, 1640, 1440, 990, 965, 910; ^{1}H NMR ($CDCl_3$) δ 5.9–5.2 (m, 3 H), 5.1 (br s, 1 H), 4.9 (m, 1 H), 2.7–2.5 (m, 1 H), 2.5–2.3 (m, 2 H), 2.3–2.1 (t, J = 6 Hz, 2 H), 1.7 (d, J = 5 Hz, 3 H); MS, m/e calcd (M^+) 138.1044, obsd 138.1038.

Anionic Rearrangement of 62. An oil-free suspension of potassium hydride (from 0.25 g of 23.6% in oil, 1.4 mmol) in 15 mL of anhydrous hexamethylphosphoramide was stirred under nitrogen at ambient temperature while **62** (0.21 g, 1.1 mmol) was added via syringe. The dark brown solution was heated to 100 °C for 12 h, cooled, and poured into ice and water (25 mL). The product was extracted into ether, washed with brine, dried, and concentrated in vacuo. Filtration through silica gel (10% ethyl acetate–petroleum ether eluant) gave a light yellow oil that was further purified by HPLC on silica gel (same solvent system). There was obtained 0.029 g (14%) of **63** as a colorless oil: IR (film, cm^{-1}) 3060, 3040, 2920, 1730, 1605, 1500, 1455, 965, 745, 700; ^{1}H NMR ($CDCl_3$) δ 9.5 (t, J = 2 Hz, 1 H), 7.2–7.0 (m, 5 H), 5.4–5.2 (m, 2 H), 3.1–2.5 (m, 3 H), 2.4 (dd, J = 2 and 6 Hz, 2 H), 1.6 (d, J = 5 Hz, 3 H); MS, m/e calcd (M^+) 188.1201, obsd 188.1206.

A degassed sample of **62** (0.15 g, 0.9 mmol) in 250 μL of benzene-d_6 was sealed in vacuo in a thick-walled ^{1}H NMR tube and heated at 220 °C for 2 h. The solution showed no evidence of formation of **63** (VPC and NMR analysis). The reaction mixture consisted primarily of dehydration products and a tarry residue and was therefore not characterized further.

Acknowledgment. The financial support of the National Institutes of Health (Grant AI-11490) is gratefully acknowledged.

Registry No. 1, 36444-19-6; 1 K^+, 82167-86-0; 1 Na^+, 82167-87-1; 1 Li^+, 82167-88-2; **4**, 1901-34-4; **6**, 74794-09-5; **7**, 1121-63-7; **8**, 82167-89-3; **10**, 61686-83-7; 11, 62163-78-4; **14**, 6731-21-1; **15**, 82167-90-6; **15** K^+, 82167-91-7; **16**, 74786-28-0; **17**, 82167-92-8; **18**, 82167-93-9; **19**, 79599-73-8; **20**, 74272-18-7; **22**, 82167-94-0; **23**, 82167-95-1; **24**, 82167-96-2; **25**, 82167-97-3; **26**, 82167-98-4; **28**, 68255-09-4; **29a**, 80534-40-3; **29a** Na^+, 82167-99-5; **29a** K^+, 82168-00-1; **29b**, 80534-41-4; **30**, 80541-08-8; **31**, 80534-44-7; **32**, 80534-42-5; **33**, 80534-43-6; **34**, 80534-45-8; **35**, 80534-46-9; **36a**, 80534-47-0; **36b**, 82168-01-2; **37a**, 80534-48-1; **37a** tosylhydrazone, 82168-02-3; **37b**, 82168-03-4; **38**, 80534-49-2; **39**, 82168-04-5; **40**, 82168-05-6; **41a**, 79599-59-0; **41b**, 82168-06-7; **41c**, 79599-60-3; **41d**, 79599-61-4; **41e**, 79599-74-9; **41f**, 79599-63-6; **41g**, 79599-62-5; **42a**, 79599-68-1; **42c**, 79599-69-2; **42d**, 79599-70-5; **42f**, 79599-71-6; **42** 2-isopropyl, 82168-07-8; **42** 2-isopropyl *N*-methyltriazolinedione, 82168-08-9; **43a**, 79599-64-7; **43c** (R_1 = CH_3; R_2 = H), 79599-65-8; **43d**, 79599-66-9; **43g** (R_1 = Ph; R_2 = H), 79599-67-0; **44a**, 80534-50-5; **44c**, 82168-09-0; **44d**, 82168-10-3; **44f**, 82168-11-4; **45a**, 82189-57-9; **46a**, 82189-58-0; **47**, 79599-75-0; **57**, 82168-12-5; **58**, 82168-13-6; **59**, 17102-64-6; **60**, 82168-14-7; **62**, 82168-15-8; **63**, 82168-16-9; 3-cycloheptenone, 1121-64-8; 3-cyclooctenone, 4734-90-1; *cis*-3-cyclononenone, 38397-25-0; 2-cycloheptenone-*5-d*, 82168-17-0; *cis*-(2-vinylcyclopentyl)acetic acid, 82189-59-1; 1-methylcyclononanol, 40001-61-4; 1-ethyl-*cis,cis,cis*-2,5,7-cyclononatrien-1-ol, 82168-18-1; 1-methoxy-1-methyl-*cis,cis,cis*-2,5,7-cyclononatriene, 80534-51-6; *N*-methyltriazolinedione, 13274-43-6; bicyclo[4.3.1]decane, 282-53-1; sorbaldehyde, 142-83-6; methyl *cis,trans*-2,4-hexadienoate, 6932-46-3.

(36) (a) Kuhn, R.; Jerchel, D. *Chem. Ber.* **1943**, *76*, 413. (b) Eisner, U.; Ellridge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1953**, 1372.