Competitive Sigmatropic Hydrogen Shifts in Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehydes[1]

John C. Gilbert* and Kenneth R. Smith

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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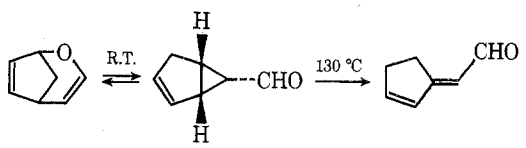
4-*exo*-Methyl- and 2-methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**1b** and **12**, respectively) each rearrange thermally to a mixture of (*E*)-2-methyl- and (*E*)-3-methyl-2-cyclopenten-1-ylideneacetaldehyde (**23** and **24**, respectively). The ratio of **24:23** obtained from **1b** is ~10, whereas that from **12** is ~0.2. Mechanistic evidence is presented that supports the conclusion that the formation of the mixture of aldehydes is a consequence of competition between concerted homodienyl [1,5] and homotrienyl [1,7] hydrogen migrations that initiate the reaction. The kinetic preference for the latter mode of rearrangement is rationalized on the basis of the relative energies of the molecular orbitals involved in the two different sigmatropic processes.

In 1968, Bickelhaupt et al.[2] reported that bicyclo[3.1.0]-hex-2-ene-6-*endo*-carboxaldehyde (**1**), which at ambient temperatures is in equilibrium with 2-oxabicyclo[3.2.1]octa-3,6-diene (**2**),[3] rearranged at elevated temperatures to (*E*)-2-cyclopenten-1-ylideneacetaldehyde (**3**). They provided



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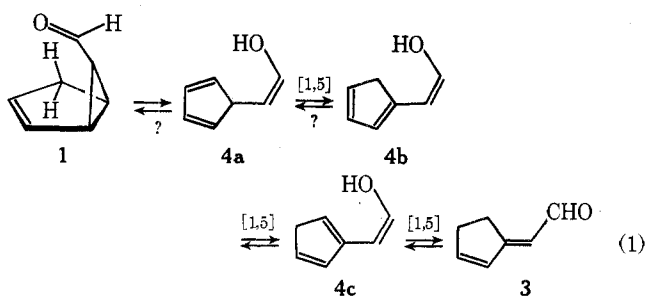
evidence that the reaction proceeded by way of the sequence shown in eq 1 by trapping isomers **4b** and **4c** with dimethyl acetylenedicarboxylate. Furthermore, **4b** and **4c** could also

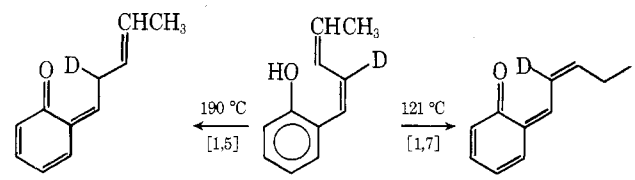


1 4a 4b 4c 3 (1)

be generated from **3**, demonstrating thereby the reversibility of the last two 1,5-hydrogen shifts.

At the time of their report, there existed ample precedent that suggested that the first step in the scheme, viz., conversion of **1** to **4a**, reasonably could occur via a homodienyl [1,5] hydrogen shift;[4] homotrienyl [1,7] hydrogen migrations were then unknown. However, it appeared to us that **1** might well be rearranging by competing homodienyl [1,5] and homotrienyl [1,7] sigmatropic pathways, even though orbital orientations (vide infra) might suppress the importance of the latter process.

There is a paucity of data in the literature that bears on the possible relationship between the rates of competing sigmatropic reactions of a specific type, e.g., hydrogen migration, and the respective orders of these reactions, although there is some evidence suggesting that the higher order pathway is kinetically favored.[5] Thus, the diene **5** appears to undergo [1,7] hydrogen migrations at 121 °C to produce **6**, but it is only after being heated to 190 °C that **5** can be induced to undergo a [1,5] hydrogen shift to produce **7**.[5a] Certainly to the extent that the transition state for a sigmatropic hydrogen migration can be characterized as a hydrogen atom interacting with the termini of the π system over which the transfer is occurring, and if other factors such as strain and steric effects are neglected,

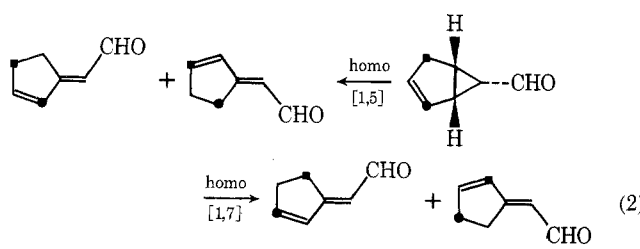


7 5 6

molecular orbital theory would predict greater stability for the transition state affording the more delocalized π system. The obvious consequence of this is that for two competing processes of different order, the higher order pathway would be kinetically preferred.

There clearly are conformational factors as well as significant differences in product stabilities that hamper definitive interpretation of the meaning of the greater rate in **5** of the [1,7] hydrogen shift as compared to the [1,5] process. In this context, the possibility of the two analogous pathways operating in the rearrangement of **1** appeared all the more interesting because their existence would provide an excellent opportunity to evaluate the relative rates of competing sigmatropic reactions in a substrate in which gross steric and conformational factors, as far as can be evaluated from molecular models, were equivalent and in which differences in stabilities of initially formed products could be minimized. Thus an investigation was undertaken to test for the possible existence of competing modes of rearrangement of bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehydes.

The conceptalization of derivatives of **1** appropriate for a differentiation of a homodienyl [1,5] from a homotrienyl [1,7] hydrogen migration in the ring-opening reaction described above is uncomplicated. Clearly, a label at either C-2 or C-4 (or at C-1 or C-5) would introduce the molecular asymmetry necessary to make the products of the two pathways distinct (eq 2). A methyl group was chosen as the label in this work



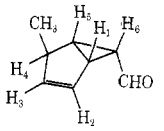
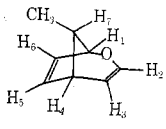
(2)

both to facilitate the synthesis of the desired substrates and to minimize perturbations in the basic bicyclic system.

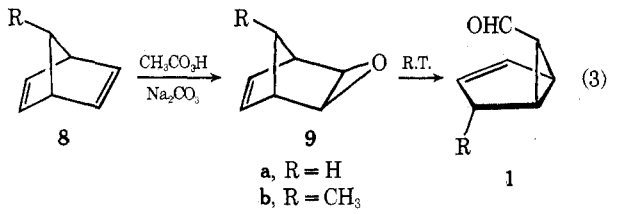
Results

Synthesis of Bicyclic Aldehydes. A facile entry into the bicyclo[3.1.0]hex-2-ene ring system has been reported by

Table I. ^{1}H NMR Data for 1b and 10

Compd	Chemical shift (δ), multiplicity [coupling constant, Hz]								
 1b	CH_3	H_1	H_5	H_6	H_2	H_3	H_4	H_7	CHO
	1.10 d [7.0]	1.64–2.65 m			5.91 t [2.0]		2.85 dq [7.0, 2.0]	—	9.12 d [6.5]
 10	0.87 d [7.0]	4.42 bs	6.26 m	5.16 m	5.67 m	4.95 t [6.0]	2.0–2.65 m		

Meinwald et al.[6] These workers found that reaction of bicyclo[2.2.1]hepta-2,5-diene (**8a**) with buffered peroxyacetic acid afforded bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**1a**), and provided evidence that implicated the epoxide **9a** as the precursor to **1a** (eq 3).[7] It was felt that application of this re-



(3)

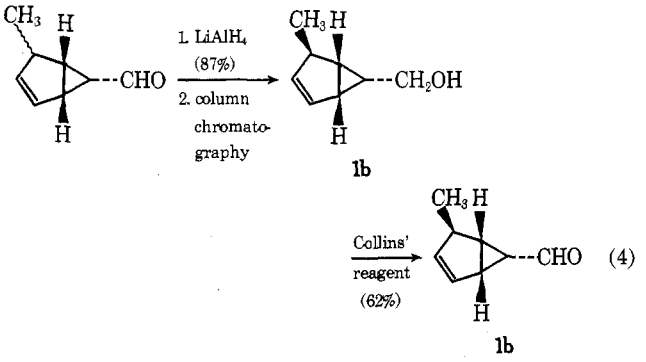
8 **9** **1**

a, R = H
b, R = CH_3

action to 7-methylbicyclo[2.2.1]hepta-2,5-diene (**8b**) might initially provide **9b** which, in turn, would isomerize to a bicyclic aldehyde, viz., 4-*exo*-methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**1b**), suited to our purposes. Of course, such an outcome required that peroxidation occur not only stereoselectively exo but also regioselectively anti to the 7-methyl substitutent. The former requirement has ample precedent in Meinwald's work[6] as well as in that of others,[8] whereas the latter is supported by the observation that introduction of a *syn*-7-methyl group in the bicyclo[2.2.1]-hept-2-ene system retards the rate of epoxidation by a factor of ca. 100 relative to the unsubstituted compound.[9] Consequently, a synthetic approach to **1b** via **8b** appeared highly attractive.[10,12]

In fact, peroxidation of **8b** afforded, in 62% yield, a 3:1 mixture of an aldehyde and two contaminants; we did not characterize the latter compounds, but they have been identified by Padwa and Koehn as the two endo epoxides that can be formed from **1b**.[11] Attempts at achieving separation of the crude reaction mixture by either GLC or column chromatography were unsuccessful owing to the extensive polymerization and/or decomposition that attended these techniques. Consequently, a chemical approach to purification was first developed, although it ultimately was discovered that the desired aldehyde could be isolated by low-temperature (−78 °C) fractional crystallization. The chemical sequence involved reduction of the reaction mixture with lithium aluminum hydride, column chromatographic isolation of the desired alcohol, and regeneration of the aldehyde function by oxidation with Collins' reagent (eq 4).[14] That structural rearrangement had not attended the purification sequence outlined in eq 4 was demonstrated by the identity of the ^{1}H NMR spectrum of the aldehyde isolated in this manner with that of the aldehyde obtained by low-temperature fractional crystalization.

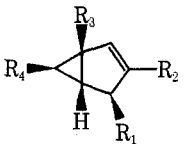
The assignment of structure **1b** to the aldehyde is based on the method of synthesis and spectroscopic analyses. Although the complete data for the assignment are contained in the Experimental Section, a summary of the arguments will be presented here. The ^{1}H NMR spectrum of **1b** is consistent



(4)

1b

with that expected for bicyclo[3.1.0]hex-3-ene-6-*endo*-carboxaldehyde as resonances assignable both to it and to the homo-oxy Cope rearrangement product, **10**, expected[3,15] to be in equilibrium with it are present (Table I). Integration of the methyl resonances revealed a ratio of **1b:10** of 3. The endo configuration of the aldehyde moiety is assigned by analogy to the observations of Meinwald et al.[6] and of Klumpp et al.[3,15] by the shift upfield of the formyl proton of **1b** by 0.3 ppm relative to cyclopropanecarboxaldehydes,[16] as a result of the shielding effect of the double bond, and by the existence of the equilibrium between **1b** and **10**. Finally, the all-important assignment of the C-4 methyl group as exo is based on the following considerations: (1) Aldehyde **1b**, the major product of peracid oxidation of 7-methylbicyclo[2.2.1]hepta-2,5-diene (**8b**), is expected on stereochemical grounds to result from epoxidation anti to the 7-methyl group, the ultimate consequence of which is exo stereochemistry for the methyl group of **1b**. (2) The coupling constant, J_{H4-H5}, is 0–2 Hz, a magnitude in accord with that predicted from the Karplus equation[17] for vicinal coupling between hydrogens at a dihedral angle of ca. 90°, and a value observed in the closely analogous compounds, **11a**[18] and **11b**.[19] (3) The chemical shift of the



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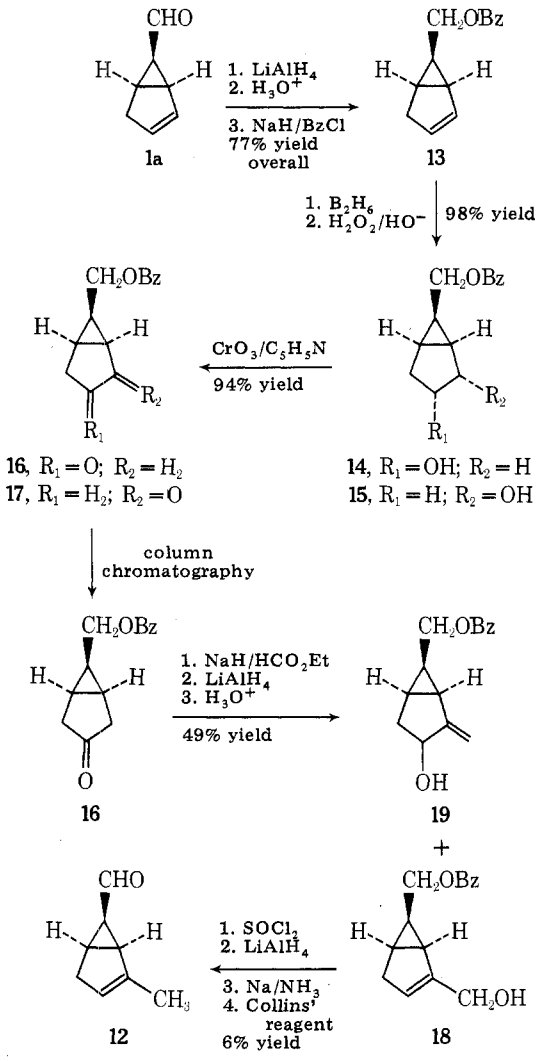
a, $R_1 = CH_3$; $R_2 = R_4 = H$; $R_3 = i$-Pr
b, $R_1 = R_2 = R_4 = Ph$; $R_3 = H$

methyl group is insensitive to the transformation of the functionality at C-6 from the alcohol (δ 1.0 ppm) to the aldehyde (δ 1.1 ppm) or the acetate (δ 1.0 ppm). (4) The propensity for thermal rearrangement (vide infra). All these data are in accord with structure **1b**.[20]

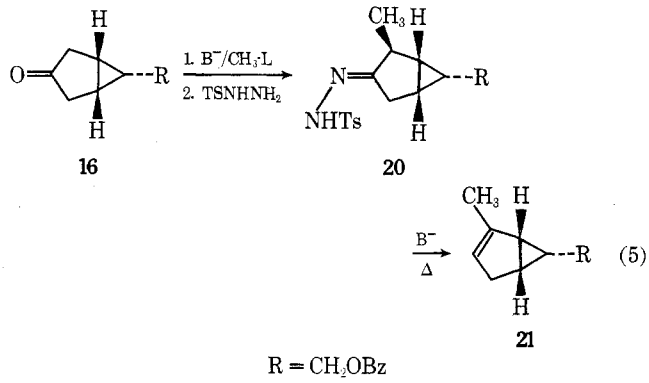
The considerably more complex scheme employed for synthesis of 2-methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**12**) is outlined in Chart I. The evidence sup-

Chart I. Synthesis of 2-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (12)



porting the structural assignments is contained in the Experimental Section, and only some of the more salient features of the synthesis will be described here. The aldehyde moiety of **1a** was protected as the benzyl ether since attempts at acetal formation under either protic or aprotic conditions led, in our hands, to a variety of uncharacterized products. The hydroboration of **13** to produce a mixture of alcohols **14** and **15**[21] was, as anticipated,[22] somewhat regioselective as judged by ir and ^{1}H NMR spectra of the ketones **16** and **17** obtained from the alcohols by Sarett oxidation.[23] Thus, the major product had $\nu_{C=O}$ 1739 cm^{-1}, a value consistent with a nonconjugated cyclopentanone,[24] and possessed high molecular symmetry as adjudged from its ^{1}H NMR spectrum: the exo and endo protons at C-2 and C-4 were revealed as an AB quartet, J_{gem} = 19.5 Hz, and the low-field half of this quartet, which represents the exo protons, was split into a pair of doublets, J_{vic} = 5 Hz, by coupling with the protons on C-1 and C-5; furthermore, the C-7 protons showed magnetic equivalence, appearing as a sharp doublet. In contrast, the minor product had $\nu_{C=O}$ 1723 cm^{-1}, a frequency consonant with the presence of a five-membered ring ketone conjugated with a cyclopropane ring,[24] and provided a ^{1}H NMR spectrum devoid of evidence of molecular symmetry; e.g., the aliphatic protons at C-1, C-3, C-4, and C-5 appeared as a broad multiplet, and the diastereotopic protons at C-7 were now a broad, rather than sharp, doublet. Consequently, these data support the contention that the major product, present in a 2:1 ratio relative to **17**, was the desired ketone **16**. The ketones could be separated by either fractional distillation or column chromatography.

It had originally been envisioned that **16** could be transformed to a precursor, **21**, of **12** by alkylation followed by base-induced decomposition of the tosylhydrazone, **20** (eq 5).[25] However, our initial lack of success at monoalkylating

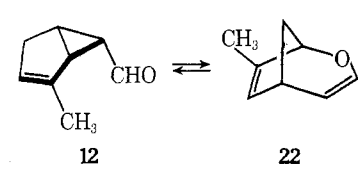


(5)

16 [*t*-BuO$^-$/MeOTs/DMF (polyalkylation) and Stork–Dowd imine alkylation[26] (lack of deprotonation of the imine suspected)] encouraged us to pursue the route shown in Chart I.[27] The ratio of allylic alcohols, **18** and **19**, formed by reduction of the α-hydroxymethylene ketone obtained from **16**, was ca. 9:1 as shown by integration of the vinylic and aromatic regions of the ^{1}H NMR spectrum of the crude mixture. Treatment of the mixture of alcohols with thionyl chloride followed by reduction with lithium aluminum hydride afforded **21** (eq 5) in 41% yield. In accord with the structure assignment, the ^{1}H NMR spectrum of **21** revealed an allylic methyl group at δ 1.75 as a broad singlet and a single vinyl proton at δ 4.4–5.2 ppm as a broad multiplet.

The deprotection of **21** was accomplished in 44% yield by reduction with sodium in liquid ammonia, and the resulting alcohol, without purification, was oxidized to the desired bicyclic aldehyde, **12**, with Collins' reagent.[14] The isolated **12** proved to be contaminated with ca. 20% of two other aldehydes as shown by ^{1}H NMR analysis, and owing to the sensitivity of **12** to mild acids, bases, and oxygen, further purification could not be achieved.

Evidence for the assignment of the aldehyde as 2-methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**12**) rests on spectral analysis and on the fact that **12** thermally rearranges to a mixture of the same two products as are obtained from the isomeric aldehyde **1b** (vide infra). In analogy with **1b** the ^{1}H NMR spectrum of **12** supports the existence of an equilibrium between the bicyclic aldehyde and its homo-oxy Cope isomer (**22**, eq 6) although the presence of impurities make an

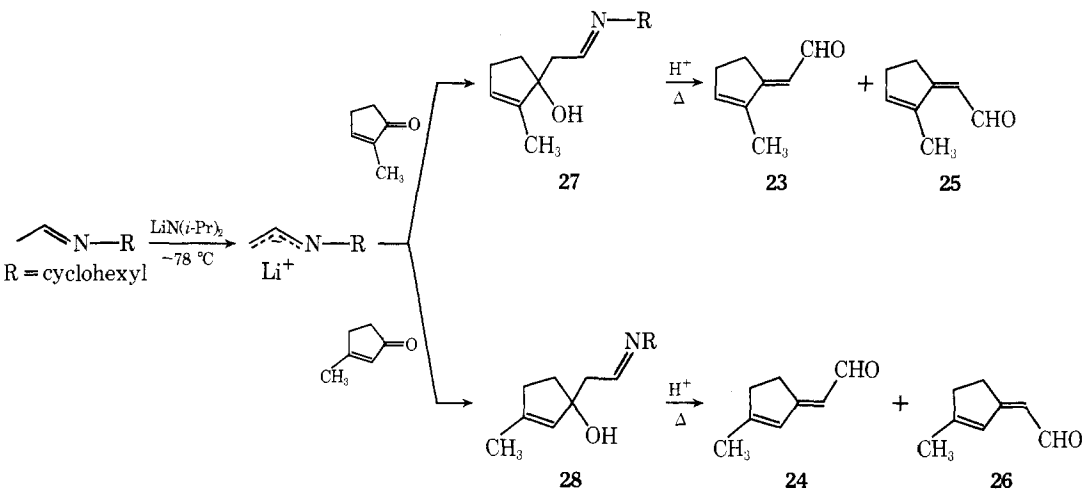


(6)

accurate assessment of the equilibrium impossible in this case. Thus, **12** is characterized by a doublet (J = 6.5 Hz) at δ 9.1 (CHO), narrow multiplets at δ 5.4 (vinyl) and 1.8 (methyl), and a broad, unresolved multiplet at δ 0.8–2.8 ppm, whereas **22** is revealed by multiplets at δ 4.6 (H_1), 5.0 (H_4), 5.7 (H_2), 6.0 (H_5); the H-4 and H-7 protons are buried in the broad multiplet centered at ca. δ 2 ppm.

Synthesis of Rearrangement Products. By analogy to the report of Bickelhaupt et al.,[2] the major products of the thermal rearrangement of aldehydes **1b** and **12** were anticipated to be (*E*)-2-methyl-2-cyclopenten-1-ylideneacetaldehyde (**23**) and (*E*)-3-methyl-2-cyclopenten-1-ylideneace-

Chart II. Synthesis of Expected Rearrangement Products



taldehyde (**24**), respectively. Authentic specimens of these two products were readily prepared by application of the "directed aldol condensation", developed by Wittig and Frommeld,[28] to 2- and 3-methylcyclopent-2-enone, respectively (Chart II). Thus treatment of these ketones with the anion of *N*-cyclohexylacetaldehydeimine afforded the corresponding β-hydroxy imines **27** and **28** in 70% yield. Hydrolysis and dehydration of these hydroxy imines and isolation of the resulting unsaturated aldehydes were accomplished in one step by steam distillation in the presence of oxalic acid.

Treatment of **27** in this manner afforded, in 55% yield, a mixture of two aldehydes in a ratio of ca. 90:10. The structure of the major component was tentatively assigned as the *E* isomer **23** on the expectation that the method of synthesis would provide the thermodynamically more stable isomer. ^{1}H NMR analysis of the reaction mixture supported this conclusion and provided evidence over and above the method of synthesis for the gross structure of **23.** Thus, the aldehydic proton appeared as a doublet at δ 9.78 (J = 7.5 Hz), the ring vinylic proton as a broad singlet at δ 6.00, the exocyclic vinylic proton as a doublet of triplets with fine splitting at δ 5.76 (J = 7.5, 2 Hz), and the remaining protons as multiplets at δ 2.70 (H_5), 3.20 (H_4), and 1.57 ppm (CH_3). The assignments were supported by decoupling experiments in the following way: saturation of the aldehydic resonance at δ 9.78 collapsed the resonance at δ 5.76 to a triplet; irradiation at this latter frequency converted the six-line multiplet at δ 3.20 to a lopsided triplet; and, finally, decoupling of the resonance at δ 3.20 considerably sharpened the broad singlet at δ 6.00 ppm. Furthermore, the resonance for the aldehydic proton of the minor isomer was deshielded by 0.06 ppm relative to the major component of the mixture. Such deshielding suggests that this aldehydic proton is in the deshielding cone of the double bond of the cyclopentyl ring, as would be expected if the minor isomer were assigned the *Z* configuration.

The analogous hydrolysis and dehydration of hydroxy imine **28** also yielded a mixture of two aldehydes in a ratio of ca. 60:40. The major isomer was again assigned the *E* configuration, i.e., structure **24,** on the basis that the aldehydic and vinylic protons were deshielded by 0.06 and 0.8 ppm, respectively, relative to the major isomer. Additionally, examinations of models suggested that there is less steric compression between the aldehyde moiety and the C-5 hydrogens of the ring than between the vinyl hydrogen of the ring and the aldehyde group.[29]

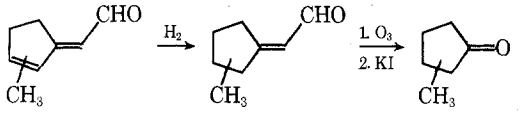
Thermal Rearrangements. A dilute solution of **1b** in a 9:1 mixture of hexane and tetrahydrofuran was first degassed and then heated in an evacuated, sealed Pyrex ampule at 160 °C for 12 h. Under these conditions, a 90% yield of rearranged aldehydes was obtained. That the product mixture was constituted of the α,β,γ,δ-unsaturated aldehydes **23** and **24** was shown by GLC and ^{1}H NMR analysis. Furthermore, integration of the areas of the respective GLC peaks showed that **23** predominated over **24** by a factor of ca. 9:1, a fact that was consonant with the observation that the ^{1}H NMR spectrum of the mixture was essentially superimposable with that of **23.**[30,31]

Table II. Analyses of Thermolysis Mixtures

Run	Substrate	Temp, °C[a]	Time, h	23, %	24, %
1[b]	**1b**	130	48	91	9
2[c]	**1b**	130	48	92	8
3[c]	**1b**	130	48	91	9
4[c]	**1b**	160	12	88	12
5[c]	**1b**	160	12	89	11
6[c]	**12**	130	48	18	82
7[b]	**24**	135	12	0	100[d]

[a] Temperature fluctuation during an individual run was ca. ±4 °C. [b] Analysis via hydrogenation–ozonolysis sequence with quantitation by GLC; maximum error is estimated to be ±1%. [c] Analysis via GLC; maximum error is estimated to be ±2%. [d] A small amount of polymerization was the only observable reaction.

Because the GLC peaks of **23** and **24** were broad and resolution of them was not complete, a second method of analysis of the thermolysis mixture was developed. This method involved catalytic hydrogenation of the more labile γ,δ π bond of the cyclopentene ring followed by reductive ozonolysis of the remaining double bond (eq 7). The mixture of 2- and 3-



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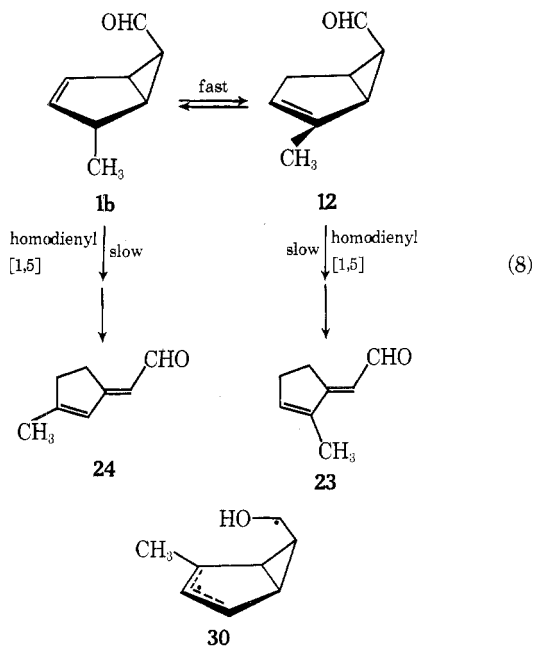
methylcyclopentanones (**29**) that resulted was then readily analyzed by GLC techniques. The results of this method of analysis as well as of the direct GLC analysis of the unsaturated aldehydes **23** and **24** are collected in Table II.

Runs 1–3 clearly illustrate the reproducibility of the analytical techniques, and runs 6 and 7 demonstrate that the rearrangement is under kinetic rather than thermodynamic control, i.e., equilibria of the type **1b** ⇄ **12** and **1** ⇄ **4a** (eq 1) are not established under the reaction conditions. The slight dependence of the product ratio on temperature is shown by runs 4 and 5.

Owing to the limited quantities of the isomeric starting aldehydes **1b** and **12**, an extensive investigation of the homogeneity of their thermal rearrangements was not possible. However, such studies were carried out on a model system, the unmethylated aldehyde **1a**. Thermolysis of **1a** under conditions identical with those used for rearrangement of **1b** and **12** except for addition of catalysts showed that both acidic (protic and aprotic) and basic (pyridine) catalysts promoted polymerization and rearrangement reactions that were not observed in the uncatalyzed thermal process. These observations, combined with the previously reported kinetic study of the rearrangement of **1a**,[1] support our belief that the thermal isomerizations of **1b** and **12** are homogeneous, unimolecular pocesses.

Discussion

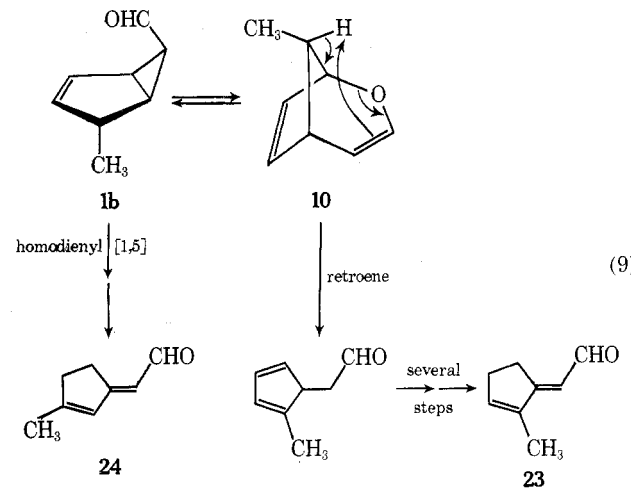
The observation of a mixture of aldehydes **23** and **24** upon thermolysis of **1b** (runs 1–5, Table II) can be rationalized mechanistically in several ways, as the following discussion illustrates; fortunately, our results appear consistent with only a single mechanistic concept. One possible mechanism invokes a rapid preequilibrium between **1b** and **12**, possibly via participation of the carbonyl oxygen, followed by rate-determining homodienyl [1,5] hydrogen shifts (eq 8). This pathway



(8)

to products is rendered untenable by comparison of the product ratios from runs 1–3 with that from run 6. Obviously, the proposal of this rapid preequilibrium would prompt the prediction that the ratio of **23** and **24** be essentially independent of whether **1b** or **12** was the starting aldehyde. This prediction is dramatically refuted by the results.

A second mechanism that accounts for formation of **23** and **24** from **1b** involves competition between a homodienyl [1,5] shift and an intramolecular retroene reaction from **10** (eq 9). However, examination of molecular models suggests that there is little, if any, overlap between the C-8 hydrogen atom of **10** and the π bond syn to it, whereas the C-4 hydrogen atom of **1b** can lie within the van der Waals radius of the carbonyl π bond. Yet the observed product radio would require the former process to dominate kinetically over the latter were this mechanism to be operating. Another factor that appears to militate against such a combination of processes is the considerable difference between the known energy of activation (42–45 kcal/mol)[32,33] of the retroene reaction that converts vinyl isopropyl ether to propane and acetaldehyde, and the



(9)

energy of activation of 29.3 kcal/mol reported for the conversion of **1a** to **3**.[1] The observed difference of some 13–17 kcal/mol in energies of activation cannot easily be accounted for by favorable strain or geometrical factors present in the bicyclic system relative to the acyclic model. Thus, although this more complex mechanism rationalizes the formation of the two aldehydes **23** and **24**, it appears to account neither for the ratio of the two products nor for the energy of activation for rearrangement of a substrate, **1a**, that is extremely analogous to **1b** and **12**.

The thermolysis results recorded in Table II, therefore, seem most appropriately interpreted as being the consequence of kinetically competitive homodienyl [1,5] and homotrienyl [1,7] hydrogen migrations. That the mode of opening of the cyclopropyl ring is kinetically controlled is shown by the fact that **1b** and **12** produce such markedly different ratios of products under identical reaction conditions and by the observation that one of the rearrangement products, **24**, is stable to the reaction conditions. It is possible, therefore, to exclude establishment of an equilibrium that interconverts **1** and **4a** (eq 1), a possibility that previously had been untested, and the intervention of which would make the reaction subject to thermodynamic control. Furthermore, the strong dependence of product ratio upon whether **1b** or **12** is the substrate for the thermolysis conclusively excludes the generation of common intermediates, e.g., **30**, that might be anticipated were the rearrangement to be stepwise in nature and supports the contention that the reaction is initiated by transfer of the endocyclic allylic proton to the carbonyl oxygen *in concert* with irreversible cyclopropyl ring opening.

Our data show the homotrienyl [1,7] hydrogen migration to be kinetically favored over the homodienyl [1,5] process by a factor of 8–10. If it is assumed that the preexponential factors for the two processes are identical, a reasonable assumption since the same geometry (see below) appears to be required for each reaction, then the [1,7] process is seen to be favored energetically by ca. 1.8 kcal/mol.

Evaluation of the basis for the energetic difference between the two pathways requires examination of the geometric and electronic features of their respective transition states. From consideration of molecular models as well as the overall course of the first step of the rearrangement (eq 1), the optimum ground state conformation for reaction is that depicted in Figure 1. As shown in Figure 1, the aldehyde moiety essentially bisects the [3.1.0] skeleton so that the aldehydic and C-6 hydrogen atoms are eclipsed, an orientation most conducive to double bond formation between their respective carbon atoms. This geometry also affords maximum overlap between the carbon–carbon bonds of the cyclopropane ring and the p orbital of the aldehydic carbon atom. An obvious consequence of this molecular geometry is that the endo hydrogen atom at

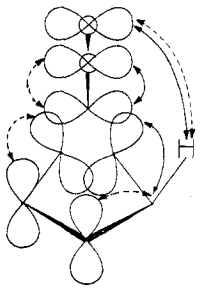


Figure 1. Reactive conformer of bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde; orbital interactions shown for homo [1,5] (—) and homo [1,7] (- - -) hydrogen shifts (see text).

C-3 is transferred to the same lobe of the p orbital on oxygen independent of whether a homodienyl [1,5] or a homotrienyl [1,7] hydrogen shift is occurring. The same basic conformation, therefore, appears ideal for both modes of rearrangement observed in the bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde system. According to this analysis, geometric factors do not account for the observed regioselectivity.

From the electronic standpoint, both modes of isomerization are "allowed" pericyclic transformations. As depicted with arrows in Figure 1, the homodienyl reaction can be characterized as $[_\sigma 4_s + _\pi 2_s]$ and the homotrienyl process as $[_\sigma 4_s + _\pi 2_s + _\pi 2_a]$.[34] The two isomerizations alternatively could be classified as having transition states corresponding to a Hückel $(4n + 2)$ and a Möbius $(4n)$ π-electron array, respectively, thereby fulfilling the requirement that thermally allowed reactions controlled by orbital symmetry possess aromatic transition states.[35,36]

Unfortunately, use of an argument based upon the relative delocalization energies of Hückel benzene and Möbius cyclooctatetraene to explain the preference for the homotrienyl process in our system is precluded by the absence of both theoretical and experimental data on the Möbius system. However, an alternate approach yields a clue to the origin of the differences in the energies of the transition states for the two competing modes of rearrangement.

This approach views the two transition states as possessing characteristics of the corresponding homodienyl or homotrienyl radicals. Although there are no experimental data available on the delocalization energies (DE) of such radicals, the estimated difference in DE between a dienyl and a trienyl radical is ca. 5 kcal/mol in favor of the latter species,[37] and some portion of this difference should apply to the corresponding homo species. Even if the full 5 kcal/mol difference applied, attenuation of this value to the 1.8 kcal/mol necessary to rationalize our results is consistent with the expectation that the transition state for hydrogen transfer with concomitant ring opening is anticipated to be more reactant- than productlike.[40]

The attenuation of the energy difference between trienyl and dienyl radicals, as measured by the ratios of products formed by homo [1,7] vs. homo [1,5] sigmatropic rearrangements in our bicyclic aldehydes, may also be partly a consequence of geometrical factors. As noted by Schakel and Klumpp,[41] the dihedral angle between the endo hydrogen atom at C-4 and the bent cyclopropyl bond between C-5 and C-6 is near 0° in the bicyclo[3.1.0] system (cf. Figure 1); this orientation of orbitals would appear to be stereoelectronically ideal for the simultaneous cleavage of these bonds, the process we believe to be occurring in the homodienyl [1,5] hydrogen shift. A similar analysis of the dihedral angle between the p orbital at C-2 and the C-1–C-6 cyclopropyl bond shows this angle as well as that between the endo hydrogen at C-4 and the p orbital at C-3 to be nonzero and leads to the conclusion that the geometries of bonds associated with the homotrienyl [1,7] process are less than ideal from a stereoelectronic standpoint. The consequence, then, is a narrowing of the energy gap between the two competing processes.[42]

It can be noted in passing that the data of Table II also suggest a slightly greater preference for the homotrienyl pathway in **1b** as compared to **12**. A potential rationale for this preference may lie in the fact that the 1,5-disubstituted cyclopentadiene initially arising from the homotrienyl rearrangement of **1b** is probably more stable than the 2,5-disubstituted cyclopentadiene resulting from the corresponding process in **12**.[43] The relative energies of the transition states for the homotrienyl rearrangement from **1b** and **12** may reflect this anticipated difference in stabilities of the products formed initially.

In conclusion, the thermal isomerization of 2-methyl- and of 4-*exo*-methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**1b** and **12**, respectively) leads to a mixture of (*E*)-2-methyl- and (*E*)-3-methyl-2-cyclopenten-1-ylideneacetaldehyde (**23** and **24**, respectively). A mechanistic analysis of these rearrangements supports the conclusion that there is a direct correlation between orbital energies and relative rates of closely analogous concerted reactions occurring via transition states having essentially identical geometries.

Experimental Section

Infrared spectra (ir) were obtained with a Beckman IR-5A spectrophotometer. Proton magnetic resonance (^{1}H NMR) spectra were recorded with either a Varian Associates A-60 or HA-100 spectrometer; all spin decoupling was performed on the HA-100. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane at 0.00 ppm. Unless otherwise noted, ^{1}H NMR data are reported in the following manner: ppm downfield from Me_4Si, number of protons, multiplicity, absolute number of the coupling constant (if measurable), and the carbon atom(s) to which the hydrogen(s) are attached (if known). The solvents for ^{1}H NMR samples were carbon tetrachloride and deuteriochloroform.

All melting points and boiling points are uncorrected with the former being taken in open capillaries with Mel-Temp apparatus.

Gas–liquid phase chromatography (GLC) analyses were performed with a Varian Aerograph A-90-P3. Helium was used as the carrier gas at a flow rate of ca. 60 ml/min unless otherwise noted, and retention times were recorded with respect to air. The following columns were used: column A, 4 m × 0.25 in., 10% Carbowax 20M on 60/80 mesh Firebrick; column B, 4 m × 0.25 in., 30% SE-30 on 60/80 mesh Firebrick; column C, 1 m × 0.25 in., 15% FFAP on 60/80 mesh Chromosorb P (acid washed); column D, 4 m × 0.25 in., 15% FFAP on 60/80 mesh Chromosorb P (acid washed); column E, 6 ft × 0.25 in., 3% SE-30 on Aeropak 30.

Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz., and Galbraith Laboratories, Inc., Knoxville, Tenn.

4-*exo*-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (1b). Oxidation of 7-Methylbicyclo[2.2.1]hepta-2,5-diene (8b).[45] A mixture of anhydrous sodium carbonate (24.3 g, 0.23 mol), dry methylene chloride (105 ml), and 7-methylbicyclo[2.2.1]hepta-2,5-diene (**8b**, 12.8 g, 0.12 mol) in benzene (approximately 12 ml) was cooled to ca. 5 °C, and peroxyacetic acid (40%, 14.5 ml, 0.09 mol), which contained anhydrous sodium acetate (0.5 g), was added at such a rate as to maintain the temperature below 15 °C. The reaction mixture was stirred for 2–3 h at room temperature (negative peroxide test) and filtered. After the filter cake was washed with methylene chloride, the filtrates were combined, dried, and concentrated in vacuo. The residue was fractionally distilled to give 6.8 g (62%) of a mixture of *exo*-methyl aldehyde, **1b**, bp 74–77 °C (30 mm), and two endo epoxides.[11]

Spectral data: ^{1}H NMR of mixture, four methyl doublets centered at δ 1.1 and 0.9 (exo aldehyde) and 1.0 and 0.83 (endo epoxides); ir 1692 cm^{-1}.

4-*exo*-Methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hex-2-ene. To a stirred slurry of lithium aluminum hydride (0.53 g, 14 mmol) in anhydrous ether (50 ml) was added the mixture from (6.8 g, 56 mmol) in anhydrous ether (25 ml). Hydrolysis was accomplished by the successive addition of water (1.6 ml), 15% sodium hydroxide (0.5 ml), and water (0.5 ml). The reaction mixture was filtered, and the filter cake was stirred with hot ethyl acetate and refiltered. The filtrates were combined and concentrated in vacuo. The light-colored residue was distilled to give 5.7 g (84%) of product alcohols, bp 68–88 °C (10

mm). The desired 4-*exo*-methyl alcohol was isolated by column chromatography with silica gel. Elution (100-ml fractions) was accomplished in the following manner.

Fractions 1–8, benzene, discard; 9–17, benzene–ether, 95:5, presumed endo epoxides (0.33 g); 18–20, benzene–ether, 95:5, 0.15 g of product. At this point the column was dismounted and its contents were extracted with ethyl acetate. The extracts were combined and concentrated in vacuo to give 4.3 g of the pure alcohol as established by GLC analysis (column A, 100 °C; column C, 100 °C; column E, 90 °C).

Spectral data: ^{1}H NMR δ 5.70 (2 H), bs [vinylic H]; 4.31 (1 H), bs [OH]; 3.30 (2 H), d, J = 7 Hz [$-CH_2O$]; 2.6–1.9 (2 H), bm [C_1–C_4 H]; 1.56–1.12 (2 H), m [C_5–C_6 H]; 1.0 (3 H), d, J = 7.0 Hz [CH_3]; ir 3400 cm^{-1} [OH].

Anal. Molecular ion, *m/e* 124.0889 (calcd for $C_8H_{12}O$, 124.0888). Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.60; H, 9.66.

Conversion of the 4-*exo*-methyl alcohol to its acetate was accomplished by addition of the alcohol (0.1 g, 8 mmol) to a solution of acetic anhydride (4 g, 40 mmol) in anhydrous pyridine (4 ml). After workup, the acetate was purified by vacuum line transfer (0.001 mm, 25 °C) and was found to be homogeneous by GLC analysis (column A, 100 °C; column C, 90 °C; column E, 90 °C).

Spectral data: ^{1}H NMR δ 5.6 (2 H), bs [vinylic H]; 3.81 (2 H), d, wfs, J = 7.5 Hz [$-CH_2O$]: 2.6–1.9 (2 H), bm [C_1–C_4 H]; 1.6–1.2 (2 H), m [C_5–C_6 H]; 1.92 (3 H), s [$CH_3C{=}O$]; 1.03 (3 H), d, J = 7.0 Hz [CH_3C_4].

4-*exo*-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (1b). The 4-*exo*-methyl alcohol (0.62 g, 5 mmol), dissolved in methylene chloride, was added dropwise (10–15 min) to a suspension of Collins' reagent[14] (10 g, 36 mmol) in anhydrous methylene chloride (200 ml). The reaction mixture was allowed to stir for an additional 30 min and was filtered. The dark filtrate was washed successively with water, 0.3 N hydrochloric acid, and saturated brine solution and concentrated in vacuo. The light brown residue was purified by vacuum line transfer to yield 0.38 g (62%) of aldehyde which was found to be subject to polymerization at room temperature.

Spectral data: ^{1}H NMR for **1b** δ 9.12 (1 H), $J \simeq 6.5$ Hz, d [HC=O]; 5.91 (2 H), unresolved t [vinylic H]; 2.86 (1 H), dq, wfs, J_{H,CH_3} = 7.0, $J_{4,5}$ = 0–2.5 Hz [C_4 H]; 1.45–2.7 (3 H), m [C_1, C_5, C_6 H]; 1.1 (3 H), d, J = 7.0 Hz [CH_3]. Ir 1692 cm^{-1} [C=O]. ^{1}H NMR for **7** δ 6.26 (1 H), m [C_6 H]; 5.67 (1 H), m [C_3 H]; 5.16 (1 H), m [C_7 H]; 4.95 (1 H), t, J = 6 Hz [C_4 H]; 4.42 (1 H), bs [C_1 H]; 2.0–2.65 (2 H), m [C_5, C_8 H]; 0.87 (3 H), d, J = 7 Hz [CH_3].

At ambient temperatures, the ratio of **1b** to **7** was found to be 3:1 by integration of the respective methyl doublets.

2-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (12).

6-*endo*-Hydroxymethylbicyclo[3.1.0]hex-2-ene. Bicyclo-[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**1a**,[6] 12.6 g, 117 mmol) was reduced with lithium aluminum hydride (1.11 g, 29.2 mmol) according to the procedure described above. Distillation provided 8.1 g (87%) of the alcohol, bp 83–85 °C (13 mm).

Spectral data: ^{1}H NMR δ 5.58 (2 H), tt [vinylic H]; 3.83 (1 H), bs ν [OH]; 3.32 (2 H), d, $J_{6,7}$ = 7.5 Hz [C_7 H]; 2.8–0.9 (5 H), m [C_1, C_4, C_5, C_6 H]; ir 3450 cm^{-1} [OH].

6-*endo*-Benzyloxymethylbicyclo[3.1.0]hex-2-ene (13). Benzylation was accomplished by a modification of the procedure of Tate and Bishop.[46] The alcohol **10** (8.1 g, 81 mmol) was added dropwise over ca. 10 min to a slurry of sodium hydride (5.6 g, 260 mmol) and anhydrous benzyl chloride (130 ml). After the addition was complete, the reaction mixture was heated to 120 °C and stirred for 3 h. After filtration of the reaction mixture and extraction of the filter cake with hexane, the combined filtrates were concentrated under reduced pressure. Fractional distillation of the residue afforded the product (89%), bp 88–90 °C (0.5 mm), which was contaminated with a small amount of benzyl chloride (GLC analysis, column E, 150 °C).

Spectral data: ^{1}H NMR δ 7.2 (5H), s [ArH]; 5.7–5.32 (2 H), m [vinylic H]; 4.36 (2 H), s [$-CH_2Ar$]; 3.21 (2 H), d, $J \simeq 7$ Hz [CH_2O]; 2.43–0.9 (5 H), bm [remaining H].

6-*endo*-Benzyloxymethylbicyclo[3.1.0]hexan-3-ol (14) and 6-*endo*-Benzyloxymethylbicyclo[3.1.0]hexan-2-ol (15). Diborane was produced by the dropwise addition of sodium borohydride (9.7 g, 256 mmol) in diglyme (270 ml) to a solution of boron trifluoride etherate (65.5 ml, 512 mmol) in diglyme (60 ml).[47] The diborane generated was carried via a stream of nitrogen into an ice-cold solution of the alkene (113.5 g, 567 mmol) in anhydrous THF (250 ml).

The reaction mixture was stirred for 10 h at room temperature and then was hydrolyzed by successive addition of water (55 ml), 3 N sodium hydroxide (88 ml), and 30% hydrogen peroxide (88 ml), while the temperature was maintained at 30–50 °C. Ether (200 ml) was added, and the reaction mixture was stirred for an additional 1 hr. The ethereal layer was decanted, and the aqueous layer was extracted with ether. The organic extracts were combined, dried ($MgSO_4$), and concentrated (aspirator) to yield 121.3 g (98%) of an oily residue which was not further purified: ^{1}H NMR, no vinylic protons.

6-*endo*-Benzyloxymethylbicyclo[3.1.0]hex-3-one (16) and 6-*endo*-Benzyloxymethylbicyclo[3.1.0]hex-2-one (17). The alcohols **14** and **15** (121.3 g, 567 mmol), dissolved in anhydrous pyridine (114 ml), were added in one portion to a mixture of chromic anhydride (114 g, 1.14 mol) and pyridine (1200 ml)[23] contained in a 2-l. Erlenmeyer, and the reaction mixture was stirred for 12 h. Ethyl acetate (500 ml) was added to precipitate the chromium salts. After an additional 0.5 h of stirring, the reaction mixture was filtered through a bed of Celite, and the filtrate was concentrated in vacuo to a volume of ca. 150 ml. The concentrate was dissolved in ether and washed successively with 3 N hydrochloric acid, 5% sodium bicarbonate, and brine solution. The ethereal extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The light-colored residue was distilled through a 10-cm Vigreux and the fraction with bp 102–130 °C (0.01 mm) was collected, 113 g (94%). However, this fraction was contaminated with some low-boiling components and contained approximately a 2:1 mixture of **16** (3-one) to **17** (2-one) as shown by GLC analysis (colunm E, 175 °C).

By repeated fractional distillation, the major product (**16**) was obtained in greater than 90% purity, 20 g, bp 130–131 °C (0.01 mm); the boiling point of **17** was higher, 132–137 °C (0.01 mm).

Separation of the two ketones was also effected by column chromatography on silica gel (50 g per gram of crude ketone) when the column was eluted in the following manner (100-ml fractions).

Fractions 1–6, benzene, discard; 7–9, benzene–ether (90:10), discard; 10–11.5, benzene–ether (85:15), 3-one (1.2 g); 11.5–12.5, benzene–ether (75:25), mixture of 3-one and 2-one (0.2 g) (2:1); 12.5–14, benzene–ether (75:25), 2-one (0.26 g).

Spectral data: ^{1}H NMR of **16** δ 7.2 (5 H), s [ArH]; 4.35 (2 H), s [benzylic H]; 3.21 (2 H), d, $J \simeq 7.5$ Hz [CH_2O]; 2.41 (2 H), dd, wfs, $J_{gem} \simeq 22.4$, $\Delta\nu_{gem} \simeq 22.4$, $J_{vic} \simeq 5$ Hz [exo C_2, C_4 H]; 2.03 (2 H), d, J_{gem} = 19.5, $J_{vic} \simeq 0$ Hz [endo C_2, C_4 H]; 1.9–0.9 (3 H), m [cyclopropyl H].

Anal. Molecular ion, *m/e* 216.1146 (calcd for $C_{14}H_{16}O_2$, 216.1150). Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.59; H, 7.75.

Spectral data: ^{1}H NMR of **17** δ 7.21 (5 H), s [ArH]; 4.43 (2 H), s [benzylic H]; 3.47 (2 H), bd, $J \simeq 7.5$ Hz [CH_2O]; 2.4–1.2 (7 H), bm [remaining H]; ir (mixture) 1739 [3-one], 1723 cm^{-1} [2-one].

2-Hydroxymethylene-6-*endo*-benzyloxymethylbicyclo-[3.1.0]hex-3-one. A modification of the procedure of Weisenborn, Remy, and Jacobs was used for hydroxymethylation,[48] Anhydrous benzene (500 ml), purified ethyl formate (33 g, 45 mmol), and sodium hydride (4.35 g, 180 mmol) were combined, and the ketone **16** (19.2 g, 89 mmol), dissolved in benzene (100 ml), was added dropwise. The resulting reaction mixture was allowed to stir under a static nitrogen atmosphere for 2 days. Excess sodium hydride was destroyed by addition of methanol (20 ml) in ether (100 ml). Water was added until all suspended solids were in solution, and the organic layer was decanted. Following extraction of the aqueous layer with ether, it was neutralized (pH 5) with 6 N hydrochloric acid and extracted with ether. The ethereal layer was washed with saturated brine, dried (Na_2SO_4), and concentrated to give an oily residue (21.7 g, 98%) that was used without further purification.

Spectral data: ir 3560–2500 and 1725–1640 cm^{-1} [hydroxymethylene ketone].

2-Hydroxymethyl-6-*endo*-benzyloxymethylbicyclo[3.1.0]-hex-2-ene (18) and 2-Methylene-6-*endo*-benzyloxymethylbicyclo[3.1.0]hexan-3-ol (19). The hydroxymethylene ketone (21.8 g, 89 mmol) in anhydrous ether (100 ml) was added dropwise to a slurry of lithium aluminum hydride (8.64 g, 220 mmol) in anhydrous ether (1 l.). After the addition was complete, the reaction mixture was stirred and heated at reflux for 8 h. Hydrolysis and workup yielded 10 g (49%) of an oily mixture of the alcohols **18** and **19** which resisted further purification.

Spectral data: ^{1}H NMR δ 5.1 [1 H], m [vinylic H]; ir 3420 [OH], 1653 and 1625 cm^{-1} [C=C].

2-Chloromethyl-6-*endo*-benzyloxymethylbicyclo[3.1.0]-hex-2-ene. The crude alcohols **18** and **19** (10 g, 43 mmol) in ether (25 ml) were added dropwise to a stirred solution of purified thionyl chloride (6.62 g, 55.6 mmol) and anhydrous ether (25 ml). After stirring the solution for 1 h, the ether was removed under reduced pressure, and the residue was subjected to a vacuum of 0.01 mm to remove trace amounts of volatile impurities. The crude product was used immediately in the next step: ir, disappearance of OH stretch.

2-Methyl-6-*endo*-benzyloxymethylbicyclo[3.1.0]hex-2-ene. The procedure of White and Gupta[27] was modified by the use of tet-

rahydrofuran rather than diisopropyl ether as solvent. The chloride(s) from above (0.043 mmol) was reduced with lithium aluminum hydride to yield, after short-path distillation, 3.8 g (41%) of products, bp 89–130 °C (0.08 mm), which was used directly in the next step.

Spectral data: ^{1}H NMR δ 7.21 (5 H), s [ArH]; 5.2–4.9 (1 H), bm [vinylic H]; 4.38 (2 H), s [OCH_2]; 1.75 (3 H), bs [allylic methyl].

2-Methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hex-2-ene. The benzyl ether (3.8 g, 14.8 mmol) in anhydrous ether (10 ml) was added to 300 ml of liquid ammonia. Sodium (1.2 g, 50 mg-atoms) was added, and the reaction mixture was stirred for ca. 30 min. The deep blue color was discharged by the dropwise addition of methanol, and the ammonia was allowed to evaporate.

Pentane (50 ml) and water (100 ml) were added to the residue, and the layers were separated. The aqueous layer was extracted with ether, and the organic extracts were combined, washed with saturated brine solution, dried (sodium sulfate), and concentrated. The residue was distilled to give 1.7 g of a colorless liquid, bp 65–99 °C (10 mm). The liquid was purified by GLC (column C, 100 °C) to give 420 mg of product (44%).

Spectral data: ^{1}H NMR δ 5.33–5.00 (1 H), m [vinylic H]; 3.81 (1 H), bs [OH]; 3.31 (2 H), m [CH_2O]; 1.8–1.6 (3 H), m [allylic methyl]; 0.8–2.7 (5 H), m [remaining H].

2-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (12). 2-Methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hex-2-ene (0.21 g, 2 mmol) was oxidized with Collins' reagent[14] (3.3 g) in methylene chloride according to the procedure described previously. The aldehyde **12** was purified by vacuum transfer (0.001 mm) at room temperature to give 65 mg of crude product, estimated to be ca. 80% pure by ^{1}H NMR analysis.

Spectral data: ^{1}H NMR δ 9.2 (1 H), d, $J \simeq 6.5$ Hz [CHO]; 5.4 (1 H), m [vinylic proton]; 1.8 (3 H), m [allylic methyl]; 2.8–0.8 (5 H), bm [remaining H].

^{1}H NMR for 7-methyl-2-oxabicyclo[3.2.1]octa-3,6-diene (**22**): δ 5.95 (1 H), m [C_6H]; 5.71 (1 H), m [C_3 H]; 5.0 (1 H), m [C_4H]; 4.6 (1 H), m [C_1 H]; 1.9 (3 H), m [allylic methyl]; 2.8–0.8 (2 H), m [C_5, C_8 H].

(*E*)- and (*Z*)-2-Methyl-2-cyclopenten-1-ylideneacetaldehyde (23 and 25). Diisopropylamine (2.0 g, 0.02 mol) in ether (10 ml) was slowly added to an ice-cold solution of anhydrous ether (40 ml) and methyllithium (11.8 ml of 1.7 M in ether, 0.02 mol). Acetaldehyde cyclohexylimine[28] (2.5 g, 20 mmol) in ether (5 ml) was added, the resulting solution was cooled to −78 °C, and 2-methyl-2-cyclopenten-1-one[49] (1.9 g, 20 mmol) in ether (10 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. Hydrolysis of the reaction mixture, followed by concentration of the organic layer provided 3.3 (75%) of the hydroxy imine **27** as a viscous oil.

A portion of this oil (1.0 g, 4.5 mmol) was dissolved in ether (50 ml), and the ethereal solution was added to oxalic acid (10 g) and water (50 ml); the mixture was rapidly steam distilled. The distillate was saturated with salt and extracted with ether. The extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Low temperature crystallization (approximately −78 °C) from ten volumes of ether provided 0.3 g (55%) of the desired aldehydes. GLC analysis (column C, 135 °C) revealed the presence of a two-component mixture with overlapping peaks with the minor isomer **25** being eluted first. The ratio of **23** to **25** was approximately 92:8.

Spectral data: ^{1}H NMR (HA-100) δ 9.78 (1 H), d: J = 7.5 Hz [CHO]; 6.00 (1 H), bs [vinylic H of cyclopentene ring]; 5.76 (1 H), dt wfs, J = 7.5, 2 Hz [vinylic H of *exo*-methylene]; 2.70 (2 H), 6-line m [H at C-5 of cyclopentene ring]; 3.20 (2 H), 6-line m [H at C-4 of cyclopentene ring]; 1.57 (3 H), 6-line m [CH_3].

(*E*)- and (*Z*)-3-Methyl-2-cyclopenten-1-ylideneacetaldehyde (24 and 26). A mixture of the aldehydes **24** and **26** was prepared from 3-methyl-2-cyclopenten-1-one[50] (20 mmol) in an overall yield of 57% by the procedure previously described for the preparation of **20** and **22.** Low temperature crystallization at ca. −78 °C from ten volumes of ether provided the two aldehydes as a low-melting (ca. 25 °C) solid which polymerized readily upon exposure to air. GLC analysis (column C, 132 °C) indicated that the ratio of **24** to **26** was approximately 60:40.

Spectral data: ^{1}H NMR of **24** δ 9.75 (1 H), d, $J \simeq 7.0$ Hz [aldehydic H]; 6.16–6.02 (1 H), m [vinylic H of cyclopentene ring]; 5.92–5.68 (1 H), m [vinylic H of *exo*-methylene]; 3.18–2.38 (4 H), m [CH_2 of cyclopentene ring]; 2.05 (3 H), bs [CH_3]. ^{1}H NMR of **26** δ 9.81 (1 H), d, $J \simeq 7.0$ Hz [aldehydic H]; 7.00–6.80 (1 H), m [vinylic H of cyclopentene ring]; 5.68–5.50 (1 H), m [vinylic H of *exo*-methylene]; 3.18–2.38 (4 H), m [CH_2 of cyclopentene ring]; 2.05 (3 H), bs [CH_3].

Thermal Rearrangements and Product Analyses. Thermolyses of **1b, 12,** and **23** were conducted on degassed samples contained in sealed Pyrex glass ampules which were heated in an aluminum-tube oven controlled by a variable transformer. The temperature of the oven fluctuated by no more than 3–4 °C during the course of thermolysis once equilibrium temperature had been established.

Thermolysis of 4-*exo*-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (1b). The thermolyses were conducted on dilute, degassed solutions of **1b** (0.5%) in hexane–tetrahydrofuran (10:1). The thermal rearrangements were conducted at 130 ± 3 and 160 ± 4 °C for 48 and 12 h, respectively.

After opening of the ampules and removal of solvent, the oily residue was purified by vacuum line transfer at room temperature (0.001 mm) to provide **23** and **24** in a yield of 90%. Analysis of the purified products was accomplished by GLC (column C, 140 °C). The products were shown to be identical with authentic samples by comparison of relative GLC retention times. Furthermore, the ^{1}H NMR spectrum of the mixture resulting from the thermolysis of **1b** at 130 °C was found to be virtually superimposable with the spectrum of an authentic sample of the 2-methyl aldehyde **23.**

Degradation of the Thermal Rearrangement Products 23 and 24. The mixture of rearranged aldehydes **23** and **24** (325 mg, 2.66 mmol) in 5 ml of ethyl acetate was hydrogenated over 10% palladium on charcoal (30 mg). After 1 equiv of hydrogen had been consumed, the solution was filtered and the filtrate was concentrated to give the α,β-unsaturated aldehydes (324 mg) in a yield of 98%.

A solution of these aldehydes (324 mg, 2.61 mmol) in chloroform–methanol was ozonized at −10 °C. The ozonolysis mixture was acidified with glacial acetic acid and reduced with excess potassium iodide solution. After reduction of liberated iodine with sodium thiosulfate, and extraction of the aqueous layer with pentane, the organic extracts were combined, dried ($MgSO_4$), and concentrated at −10 °C under aspirator vacuum to yield a mixture of 2- and 3-methylcyclopentanone (**29**). Preparative GLC (column D at 100 °C) provided pure samples of the ketones. The ir spectra of these products were superimposable with the ir spectra of authentic samples.[51] GLC retention times of these products were identical with those of authentic samples.

Thermolysis of 2-Methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (12). A degassed solution of **12** in hexane–tetrahydrofuran (10:1) was heated at 130 °C for 48 h. Removal of the solvent and purification of the residue by vacuum line transfer provided the two rearrangement aldehydes **23** and **24** which were quantitated by GLC (column C, 140 °C).

Thermolysis of 3-Methyl-2-cyclopenten-1-ylideneacetaldehyde (24). A degassed solution of **24** (0.5%) in hexane–tetrahydrofuran was heated at 135 °C for 12 h. This resulted in the formation of a small amount of polymer, but in no isomerization to **23** as evidenced by GLC analysis (column C, 140 °C).

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Registry No.—**1a,** 4729-05-9; **1b,** 35391-55-0; **7,** 60153-50-6; **8b,** 13437-93-9; **10,** 60153-51-7; **12,** 35391-56-1; **13,** 60153-52-8; **14,** 60153-53-9; **15,** 60153-54-0; **16,** 60153-55-1; **17,** 60153-56-2; **18,** 60153-57-3; **19,** 60153-58-4; **22,** 60153-59-5; **23,** 41828-82-4; **24,** 60153-60-8; **25,** 60153-61-9; **26,** 60153-62-0; **27,** 60153-63-1; 4-*exo*-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hex-2-ene, 60153-64-2; 4-*exo*-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hex-2-ene acetate, 60153-65-3; 2-hydroxymethylene-6-*endo*-benzyloxymethylbicyclo[3.1.0]hex-3-one, 60153-66-4; 2-chloromethyl-6-*endo*-benzyloxymethylbicyclo[3.1.0]hex-2-ene, 60153-67-5; 2-methyl-6-*endo*-benzyloxymethylbicyclo[3.1.0]hex-2-ene, 60153-68-6; 2-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hex-2-ene, 60153-69-7; acetaldehyde cyclohexylimine, 1193-93-7; 2-methyl-2-cyclopenten-1-one, 1120-73-6; 3-methyl-2-cyclopenten-1-one, 2758-18-1.

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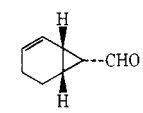

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