[1,3]-Sigmatropic Rearrangement with Retention of Configuration Forced upon the Migrating Group[1a]

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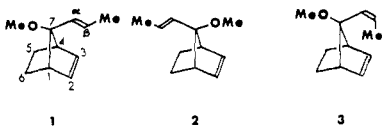
Abstract: Both the antarafacial-retention (antara-ret) and suprafacial-inversion (supra-inv) pathways of orbital-symmetry allowed [1,3]-sigmatropic rearrangement require that the geometry of many potential substrates be severely distorted in the transition state. These rearrangements therefore offer especially stringent tests of orbital-symmetry control. In an attempt to force the antara-ret reaction to occur, a series of substrates (**1**, **2**, and **3**) has been constructed in which inversion of the migrating group (the bridgehead carbon) is sterically prohibited, and the stereochemistry of the rearrangement to the enol methyl ether of **20** is deduced from the configuration of the ketone product. The endo and exo isomers of ketone **20** (**20a** and **20b**) are identified by independent synthesis (Scheme I). Pyrolyses of **1** or **2** at 254.5–289.5° followed by hydrolysis give endo isomer **20a** (>99% stereospecific) as the sole product of formal [1,3]-sigmatropic rearrangement, whereas **3** gives a mixture of 2–3 parts exo (**20b**) and 1 part endo (**20a**). The favored mechanism for the rearrangements of **1** and **2** involves the formation of a *cis*-1,2-dialkenylcyclopropane (**25**, Scheme III), which by a highly stereospecific boat-like Cope rearrangement is converted to **20a**. The completely stereospecific transformations **1** → **20a** and **2** → **20a**, which would be formally antara-ret and supra-ret, respectively, if interpreted as direct [1,3]-sigmatropic processes, probably are not involved.

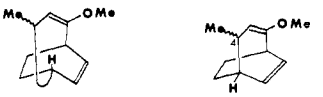
There are two possible ways of meeting the requirement[2] that an orbital symmetry allowed thermal [1,3]-sigmatropic rearrangement have a $2_s + 2_a$ orbital topology in the transition state. In one of these, the reaction occurs suprafacially on the allylic framework with inversion of configuration in the migrating group. In the other, the rearrangement is antarafacial with retention of configuration in the migrating group. The geometry of many potential substrates is inimical to such processes and requires severe molecular distortions to achieve the allowed transition state.

To investigate systematically the degree of control that orbital symmetry can exert despite such opposition, we have constructed a series of molecules in which one of the stereochemical variables is constrained and the other is tested for adherence to orbital symmetry prediction. In previous papers,[3] we studied cases in which the allylic framework was fixed so as to force suprafacial migration, while the stereochemistry of the migrating group was examined. We now report examples in which the constraint is removed from the allylic framework and transferred to the migrating group, the bridgehead carbon (C_1) of each of the three substrates, *syn*-7-*trans*-propenyl-*anti*-7-methoxynorbornene (**1**), *anti*-7-*trans*-propenyl-*syn*-7-methoxynorbornene (**2**), and *syn*-7-*cis*-propenyl-*anti*-7-methoxynorbornene (**3**).



1 **2** **3**

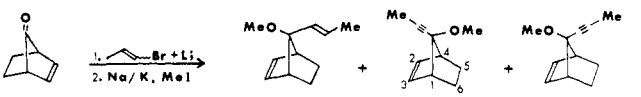
In each of these reactants, the stereochemistry at the migration terminus, C_β of the propenyl chain, would be revealed by the configuration of the C_4 methyl group in the 1,3-rearrangement product, **5**. The stereochemistry of the migrating carbon, however, perforce would be retained, since migration with inversion would lead to a highly strained trans-bridged bicyclo[3.2.2]nonene (*e.g.*, **4**).



4 **5**

Because adherence to the allowed antarafacial pathway would require that the migrating group pass through the nodal plane of the allylic system, constraint of the migrating carbon in this way would make possible a particularly stringent test of orbital symmetry. The test is still incomplete, but in the course of constructing it, we now have observed some strikingly stereospecific new rearrangements. This paper concerns these reactions and their possible relevance not only to the above mechanistic problem but also to the question of the stereodistal Cope rearrangement.

Synthesis and Rearrangement of the 7-Propenyl-7-methoxynorbornenes (1, 2, and 3). The reaction of norbornen-7-one (**6**) with a reagent prepared from lithium and 1-bromo-1-propene, followed by methylation of the resulting alcohols gave a mixture of at least three methyl ethers in relative amounts of 1:5:4. There was a minor amount of the *anti-trans*-propenyl compound (**2**), but the two major products were the acetylenic ethers **7** and **8**, which could be obtained in pure form by vapor phase chromatography (vpc).



6 **2** **7** **8**

The stereochemical assignments to **7** and **8** were

(1) (a) The support of this work by the National Institute of General Medical Sciences (GM-16962), the National Science Foundation (GP-33909X), and the Hoffman-La Roche Foundation is gratefully acknowledged. (b) National Institute of General Medical Sciences Postdoctoral Fellow (1 FO2 GM-34,242), 1969–1971.

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(3) (a) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5303 (1967); (b) **92**, 1096 (1970); (c) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968); (d) *ibid.*, **5**, 406 (1972); (e) J. A. Berson and R. W. Holder, *J. Amer. Chem. Soc.*, **95**, 2037 (1973).

Table I. Spectroscopic Properties of the 7-Propenyl-7-methoxynorbornenes

Proton	Compd (config. of propenyl group) 1 (syn, trans)	2 (anti, trans)	3 (syn, cis)
	nmr[a,c]		
1	2.64; m	2.74; m	2.80; m
2	5.95; t; 2	6.04; t; 2	5.97; t; 2
5-*endo*	0.96; m	0.96; m	0.95; m
5-*exo*	1.94; m	1.67; m	1.95; m
8	5.36; d; 16	5.36; d × d; 16, <1	5.38; d × d; 11.5, <1
9	5.67; d × d; 5, 16	5.79; d × d; 16, 5.5	5.66; d × d; 11.5, 5.5
OCH_3	3.09; s	3.03; s	3.09; s
CH_3	1.70; d; 5	1.75; d × d; 5.5, <1	1.73; d × d; 5.5, <1
	ir[b,d]		
cis HC=CH	715	703	714
trans HC=CH	963	972	

[a] Chemical shift in δ units; multiplicity; coupling constant in Hz. [b] Diagnostic "C–H bending" absorptions in cm^{-1}. [c] Solvent $CDCl_3$. [d] Solvent $CHCl_3$.

derived from pseudocontact shifted nuclear magnetic resonance spectra. Addition of incremental amounts of (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octandione)europium(III) ($Eu(fod)_3$)[4] to solutions of the ether **7** caused a selective downfield shift of the two bridgehead protons (H_1 and H_4) and two of the aliphatic ring protons (exo H_5 and H_6). The H_1 and H_4 protons again were strongly shifted downfield in **8**, but in this case the olefinic pair (H_2 and H_3) experienced a much stronger shift than either pair of H_5–H_6 protons. The reasonable assumption that coordination of europium was with the methoxyl oxygen then led to the assignments shown.

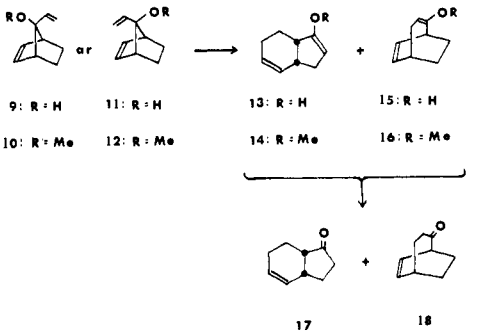
Stereospecific trans reductions of the *syn*- and *anti*-propynyl compounds **7** and **8** with sodium in liquid ammonia[5] gave the corresponding *syn-trans*- and *anti-trans*-propenyl compounds, **1** and **2**.

The *cis*-propenyl compounds proved more difficult to obtain. Several attempts to effect chemical or catalytic selective semihydrogenation of the acetylenic group of **7** or **8** gave mixtures, and, in fact, we have not yet succeeded in establishing a convenient route to the *anti-cis*-propenyl compound.

However, the *syn-cis*-propenyl isomer **3** was obtained from the mixture that resulted when norbornen-7-one reacted with the Grignard reagent from 1-bromo-1-propene. Preparative vpc separated this mixture into two major fractions, the first of which consisted of a 30:70 mixture of the above *syn-trans*-propenyl compound **1** and a new isomer in which the propenyl group clearly had the cis configuration and probably was syn to the ring double bond (**3**). The components were difficult to separate further by vpc, but the syn-cis isomer **3** could be obtained nearly pure by taking advantage of the much greater rate of pyrolysis of the syn-trans isomer (**1**). The latter component was selectively destroyed by heating the first vpc fraction, whereupon it was a simple matter to separate by vpc the unreacted **3** from the products of pyrolysis of **1**.

The configuration of **3** followed from the absence of the typical trans C–H infrared absorption in the 970-cm^{-1} region (compare the trans compounds **1** and **2**, Table I), from the near-identity in chemical shift positions of the C_5–C_6 and OCH_3 protons to those of the syn-trans isomer **1** in the nmr (Table I), and from the observation that its pyrolysis, like that of **1**, gave a high proportion of Cope rearrangement products. These data, although not sufficient to establish the stereochemistry unequivocally (particularly in the absence of the remaining anti-cis isomer), nevertheless, are strongly suggestive. It will become clear that the distinction between *syn-cis*- and *anti-cis*-propenyl compounds is not critical for the present study, as long as the configuration of the propenyl group is cis. The latter feature seems to be firmly established by the observations just described.[6]

Some close analogies for the proposed pyrolytic rearrangements of the 7-methoxy-7-propenylnorborn-2-enes were available in the previously reported reactions of the 7-hydroxy-[7a] and 7-methoxy-7-vinylnorborn-2-enes[7b] (**9**–**12**). These substances rearranged to derivatives of the bicyclo[4.3.0]- (**13**, **14**) and bicyclo[3.2.2]- (**15**, **16**) nonane ring systems by [3,3]- and [1,3]-sigmatropic rearrangements, respectively. In the methoxy series, it was possible to isolate the enol ethers (**14** and **16**),[7] but these compounds were unstable and readily hydrolyzed to the ketones (**17** and **18**). Accordingly, we expected to obtain the corresponding C-methyl derivatives (**19** and **20**) by mild hydrolytic work-up of the pyrolysis products from the propenyl compounds **1**, **2**, and **3**.



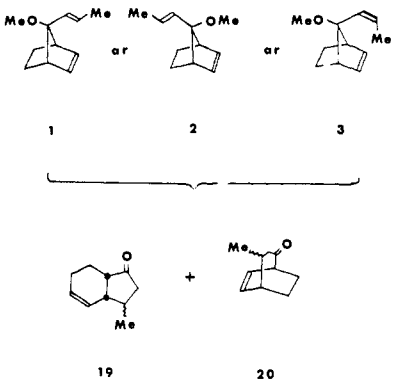
Individual preparative scale pyrolyses of these three

(4) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(5) A. L. Henne and K. W. Greenlee, *J. Amer. Chem. Soc.*, **65**, 2020 (1943).

(6) (a) It seems likely that some of our difficulties in the stereospecific syntheses of **1**, **2**, and **3** might have been avoided by the use of more efficient techniques[6b,c] for the generation and handling of the propenyllithium reagents. (b) D. Seyferth and L. G. Vaughan, *J. Amer. Chem. Soc.*, **86**, 883 (1964); *J. Organometal. Chem.*, 1, 201 (1963). (c) G. W. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

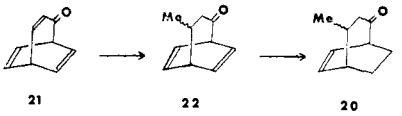
(7) (a) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5017, 5019 (1964); (b) J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90**, 4732 (1968).



compounds in the vapor phase near 300° followed by hydrolysis gave mixtures from which it was possible to isolate by preparative vpc products of both [3,3]- and [1,3]-sigmatropic rearrangement.

[3,3]-Sigmatropic (Cope) Rearrangement Products (19). The stereochemistry of the [3,3]-rearrangement product has not yet been assigned, but its gross structure as a bicyclo[4.3.0]nonane derivative (**19**) was in accord with the nmr and especially with the ir spectrum, which showed a strong cyclopentanone absorption at 5.80 μ. Both possible configurations of the methyl group of **19** seemed to result from the pyrolysis, but the proportions of the two stereoisomers formed depended on the stereochemistry of the reactant.

[1,3]-Rearrangement Products (20). The [1,3]-sigmatropic rearrangement of **1** or **2** led to a single stereoisomer **20a**. Pyrolysis of **3** gave the same ketone, **20a**, but now admixed with a second isomer, **20b**. The gross structure of **20** was confirmed as that of a bicyclo[3.2.2]nonene derivative by independent synthesis from the known[8] bicyclo[3.2.2]nona-2,6,8-trien-4-one (**21**).

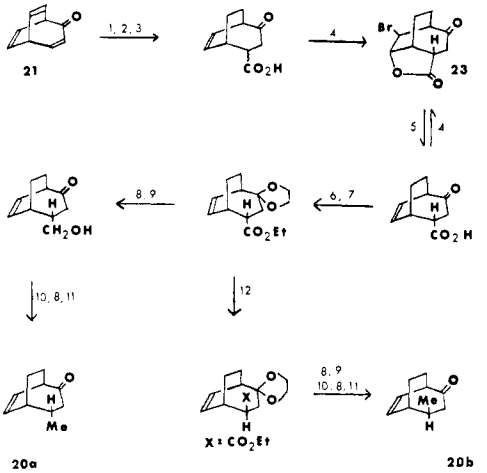


Cuprous chloride catalyzed addition of methylmagnesium iodide to **21** gave a mixture of two stereoisomeric conjugate addition products (**22**) and a small amount of tertiary alcohol.[9] Partial hydrogenation of the dienone **22** over platinum oxide in ethanol, followed by column chromatography of the product on 20% silver nitrate–silica gel, gave a mixture of the two stereoisomers of the enone **20**. One of the substances obtained by vpc separation was identical with the rearrangement product, **20a**, from the pyrolyses of **1** or **2**, and the other was identical with the second product from **3**, **20b**.

Stereochemistry of the 1,3-Rearrangements. No firm basis for the assignment of epimeric configurations to the two rearranged ketones, **20a** and **20b**, emerged from either the normal or lanthanide-induced pseudocontact-shifted nmr spectra. In the hope that a cis or trans relationship of the methyl and hydroxyl groups might be detectable and thereby stereochemically decisive, the ketones were individually reduced with lithium aluminum hydride, and the pairs of epimeric alcohols obtained in each case were separated by vpc. Three of the four alcohols were obtained pure in sufficient quantity for nmr examination of the lanthanide-treated samples. However, because the results were not wholly convincing, we sought independent confirmation by stereospecific syntheses of the two isomers, **20a** and **20b**.

The general plan was to establish by ring closure the syn relationship of the double bond and a potential methyl group in the endo series. Scheme I outlines the specific procedures used.

Scheme I[a]



[a] Reagents in Scheme I: 1, KCN, DMF; 2, OH^-, MeOH; 3, H_2, Pd/C; 4, Br_2, Na_2CO_3; 5, Zn, EtOH; 6, $C_2H_4N_2$; 7, $HOCH_2$-CH_2OH; 8, $LiAlH_4$; 9, H_3O^+; 10, TsCl; 11, CrO_3; 12, NaOEt.

The ketone **20a** obtained in the pyrolysis studies proved to be identical in all respects to the *endo*-methyl ketone synthesized from the bromolactone **23** of Scheme I, whereas ketone **20b**, the other stereoisomer from the pyrolyses, was identical with the *exo*-methyl compound obtained by the epimerization–reduction route of Scheme I.

Kinetics, Quantitative Product Distributions, and Mechanistic Implications. Pyrolyses of all three substrates, **1**, **2**, and **3**, occurred with first-order kinetics at temperatures between 254.5 and 289.5° in the gas phase in Pyrex glass tubes. Doubling the surface-to-volume ratio had no effect on the pyrolysis rate or on the composition of the products. Although small changes in the product ratios were caused by changing the pyrolysis temperatures, the ratios remained constant with time at a given temperature. These observations are consistent with a set of competing homogeneous unimolecular rearrangements. Table II gives typical distributions of the ketones obtained after hydrolysis of the enol ether pyrolysis products from these substrates.

The rate constants of the various individual processes involved (at 289.5°) are summarized in Scheme II. Each value was obtained by multiplying the overall pyrolysis rate constant by the fraction of product. Syn–anti interconversion of the two substrates **1** and **2** did not occur detectably during pyrolysis. Since the pyrolysis rates of the isomers did not differ greatly (Scheme II), any such process would have led, during the early stages of pyrolysis of one of them, to the accumulation of the other. This was not observed.

Moreover it is highly unlikely that cis–trans isomerization of the propenyl side chain was taking place during the reaction. Had this occurred in competition

(8) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).

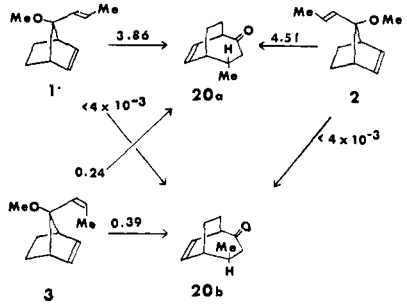
(9) We are indebted to Dr. J. Barborak and Professor P. v. R. Schleyer, who provided directions for this reaction before publication.

Table II. Pyrolysis Products from 7-Methoxy-7-propenylnorbornenes

Reactant	Temp, °C	Product, %[a] [1,3]-Sigmatropic **20a** (endo)	**20b** (exo)	[3,3]-Sigmatropic **19a**	**19b**
syn-trans-**1**[b]	289.5	27.8	0	2.0	70.2
	274.5	26.7	0	1.3	72.0
	254.5	24.4	0	1.1	74.5
anti-trans-**2**[b]	289.5	94.0	0	3.3	2.7
	274.5	95.3	0	2.2	2.5
	254.5	96.3	0	1.9	1.8
syn-cis-**3**[b]	289.5	12.8	21.2	31.6	34.4
	274.5	12.4	22.3	31.7	33.6
	254.5	8.2	23.0	33.3	35.4

[a] Per cent of product exclusive of any recovered starting material. [b] Stereochemistry of propenyl group.

Scheme II.[a] Rate Constants ($\times 10^4$ sec) of 1,3-Sigmatropic Rearrangement at 289.5°



[a] Primary pyrolysis products are enol ethers of **20a** and **20b**. The ketones are formed after hydrolysis.

with rearrangement, pyrolysis of the syn-trans compound **1** would have led to the syn-cis isomer **3**, a much less reactive pyrolysis substrate, which therefore would have accumulated in pyrolyses carried short of complete conversion. Had it occurred in a pyrolysis intermediate (for example, a diradical), the *exo*-3-methylbicyclo[3.2.2]nonene **20b**, which was a prominent product from the syn-cis reactant **3**, also should have been formed from **1**.

Finally, the product distributions of Table II were evidently kinetically controlled, since they were essentially insensitive to the extent of total conversion of the starting material.

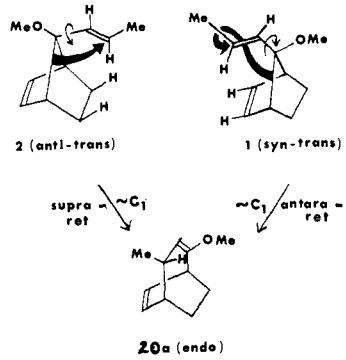
In the [3,3]-sigmatropic rearrangements, the syn-trans reactant **1** gave one of the two hydrindenones (**19b**) in heavy preponderance, but the other two substrates, *anti-trans*-**2** and *syn-cis*-**3**, gave roughly equal amounts of **19a** and **19b**. There are several possible interpretations of these results, but since the configurations of the products are not yet known, any mechanistic discussion would be speculative.

In the [1,3]-sigmatropic rearrangements, both of the substrates with *trans*-propenyl groups (**1** and **2**) gave the same product, the *endo*-methyl ketone **20a**, with extremely high stereospecificity (>99%), whereas the *cis*-propenyl substrate **3** gave a mixture of *exo*- and *endo*-methyl ketones, **20b** and **20a**, in a ratio of about 2 or 3:1.

From Arrhenius plots of the temperature dependencies of the first-order rate coefficients for overall disappearance of the two *trans*-propenyl isomers, the activation parameters for these processes were found to be (for the syn isomer **1**) $E_a = 45.4 \pm 1$ kcal/mol, log $A = 14.7$, and (for the anti isomer **2**) $E_a = 43.4 \pm 1.5$ kcal/mol, log $A = 13.5$. The indicated errors in the E_a values are larger than the statistical average deviations and represent a necessary skepticism in dealing with Arrhenius parameters derived from data at only three temperatures.

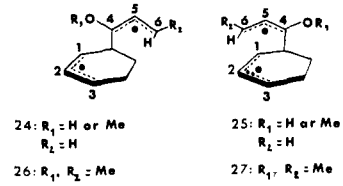
Discussion

In a formal sense, the rearrangements of the *syn-trans*-**1** and *anti-trans*-**2** compounds to *endo*-product **20a**



correspond to [1,3]-sigmatropic shifts, necessarily with retention (ret) in the migrating group, which are completely stereospecific, the reaction from **1** being antarafacial (antara) and that from **2** suprafacial (supra). If the **1** → **20a** process is interpreted as an orbital symmetry allowed ($_{\sigma}2_s + {}_{\pi}2_a \rightarrow$ antara-ret) reaction, the magnitude of the antarafacial stereospecificity (>99%) is astonishing in comparison to other examples of 1,3-rearrangements across *trans*-propenyl frameworks,[10] where the antarafacial reaction makes up only 5–11% of the total retention pathway (antara-ret + supra-ret). Similarly, the stereospecificity of the supra-ret rearrangement of **2** (again >99%) is much higher than that of most of the previous examples.[3b,d,e]

The original rationalization[7] of the results of pyrolyses of the 7-vinyl compounds **9**–**12** involved the formation and rotational interconversion of conformationally distinct diradicals, **24** and **25**. A similar



hypothesis in the present cases would involve diradicals **26** and **27**. In fact, a referee has urged such an interpretation on the ground that the observed activation energy is considerably more than the enthalpy increment estimated to be necessary to form the diradical and that this finding "can in principle be ascribed to a biradical opening in the rate-determining step."

We may estimate the endothermicity roughly as the strength of the C_2–C_3 bond in butane (81.6 kcal/mol)[11] minus the sum of the strain energy of norbornene (17–23 kcal/mol)[12] and the radical stabilizing effects of two

(10) J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 269 (1973).

(11) J. H. Purnell and C. P. Quinn, *Proc. Roy. Soc., Ser. A*, 270, 267 (1962); *Nature (London)*, **189**, 656 (1961); *Can. J. Chem.*, **43**, 721 (1965).

(12) (a) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116, 4122 (1957); (b) H. K. Hall, Jr., C. D. Smith, and J. H. Baldt, *ibid.*, **95**, 3197 (1973).

allylic groups (13 kcal/mol each)[13] and a methoxyl group (2–3 kcal/mol).[14] On this basis, the heat of formation of diradical **26** or **27** would be only 37–42 kcal/mol above that of the substrate **1** or **2**. The observed activation energies of 43–45 kcal/mol therefore *permit* a diradical intermediate. However, they do not require it, for if the energy of the transition state for formation or recyclization of the diradical were higher than that of the observed transition state, the reaction would be concerted. In other words, the enthalpic benefit of concert is the difference between the observed activation energy (E_a^{obsd}) and the activation energy for the hypothetical diradical process (E_a^R), *not* the difference between E_a^{obsd} and the endothermicity of the diradical-forming step.

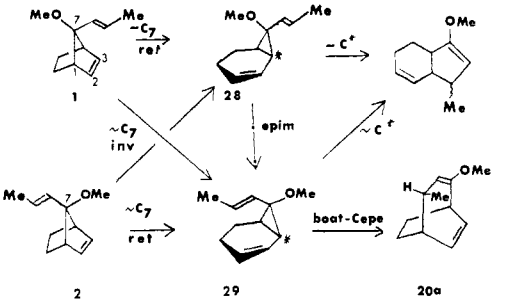
Estimates of E_a^R are notoriously uncertain. For example, there are no clear guidelines for guessing how much of the norbornene strain energy still would persist or how much of the allylic radical stabilization would be available in the diradical-forming transition state. Similar difficulties occur in many thermal reactions. In general, therefore, the activation energy is a clear-cut criterion of mechanism only when it places the transition state energy well below that of the hypothetical diradical intermediate. This relationship implies concert. A transition state energy above that of the diradical is mechanistically ambiguous.

The previous studies of the 7-vinyl compounds **9**–**12** lacked the benefit of the stereochemical label provided by the terminal methyl group of the propenyl side chain in the present work. What now has become clear is the extremely high stereospecificity of formation of the [1,3]-sigmatropic products from **1** and **2**, a phenomenon not previously detectable. Our confidence in diradicals *as the immediate product-forming intermediates* has been shaken by this observation. The formation of the observed *endo*-methyl product **20a** from diradical **27** would require a counterclockwise rotation about the C_5–C_6 bond and juncture of C_3 to the side of C_8 which is distal from the viewer. The referee has asserted in a general way that there are steric reasons for this process to be preferred over the clockwise rotation-proximal side closure of diradical **27** to the *exo*-methyl isomer **20b**. However, our own inspection of molecular models of this system has failed to provide us with a convincing rationale for predicting even the direction of any preference, not to mention its observed overwhelming magnitude.

It is therefore important to ask whether mechanisms other than those considered so far might not account for these results.[15]

One alternative (Scheme III) would involve a reversal of the roles of the two allylic systems of the reactants. Instead of the bridgehead carbon (C_1) acting as a migrating group which moves across the propenyl side chain, it is conceivable that C_7 could migrate, and the potential allylic system in the ring (C_1–C_2–C_3) could serve as the receptor moiety. For steric reasons, the latter process would necessarily occur suprafacially.

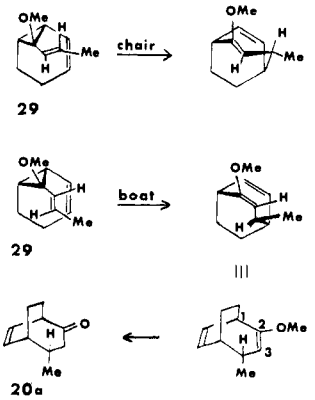
Scheme III



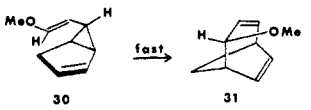
Retention of the configuration of C_7 in the rearrangement of the *syn-trans*-propenyl compound **1** would lead to a bicyclo[4.1.0]heptenyl derivative with an *exo-trans*-propenyl group **28**, whereas inversion would lead to a compound of the same ring system but with an *endo-trans*-propenyl group (**29**). The *anti-trans*-propenyl compound **2** would give **28** by inversion and **29** by retention.

Compound **29** is a *cis*-1,2-dialkenylcyclopropane derivative, and like other members of this class,[16] it should be converted rapidly by a Cope rearrangement to a 3-methylbicyclo[3.2.2]nona-2,6-diene. This rearrangement should lead by way of a transition state with a boat-like array of the biallyl system to the observed *endo*-methyl product **20a**. The reaction should occur with high stereospecificity, since the chair-like geometry normally preferred[17] in acyclic cases would lead to a highly strained bicyclo[3.2.2]nonadiene with a trans double bond (Scheme IV). A referee has called

Scheme IV



to our attention a very close analogy in the rearrangement of the *trans*-enol ether **30**, which gives the endo-



substituted bicyclo[3.2.1]octadiene derivative rapidly and exclusively.[16c]

It must be emphasized that Scheme III is noncommittal on the details of the reactions by which the *syn*-divinylcyclopropane **29** is formed. These may proceed by concerted mechanisms or by way of diradicals. In the latter case, Scheme III would differ from the mech-

(13) W. von E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973), and references cited therein.

(14) (a) J. A. Berson and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **90**, 4730 (1968); (b) A. Ohno and Y. Ohnishi, *Tetrahedron Lett.*, 4405 (1969); (c) J. W. Timberlake and M. L. Hodges, *ibid.*, 4147 (1970).

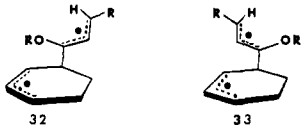
(15) We are indebted to several members of our research group, particularly J. A. Jenkins, P. B. Dervan, D. S. Kabakoff, and E. W. Petrillo, for valuable suggestions on this subject.

(16) (a) E. Vogel, *Angew. Chem.*, **72**, 21 (1960); (b) J. M. Brown, B. T. Golding, and J. J. Stofko, Jr., *J. Chem. Soc., Chem. Commun.*, 319 (1973), and references cited therein; (c) J. M. Brown, *Chem. Commun.*, 638 (1967).

(17) W. von E. Doering and W. R. Roth, *Tetrahedron*, 18, 67 (1962).

anism previously proposed for the rearrangements of the vinyl series **9**–**12** merely in the requirement that the diradical not cyclize directly to **20a**, but instead, that it collapse at C_1–C_4 to give the *syn*-divinylcyclopropane **29**, which then would rearrange rapidly to **20a**. Were it not for the strongly suggestive stereospecificity, an experimental distinction between direct cyclization of the diradical and the alternative two-step process *via* **29** would be difficult to make, because **29** undoubtedly would be too reactive to accumulate in readily detectable amounts.

In detail, one question might be raised concerning the hypothetical diradical mechanism. Why should diradical **27** cyclize exclusively between C_1 and C_4 to give the proposed intermediate cyclopropane **29** and not directly between C_3 and C_6 to give the final product **20a**? A good reason for this might be that formation of diradicals from substrate **1** or **2** with the propenyl side chain in a trans-allylic configuration (**32** and **33**)

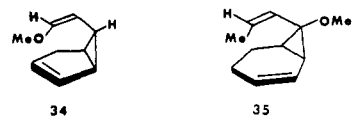


32 **33**

should be considerably faster than formation of the cis-allylic diradicals **26** and **27**. Since cis-allylic $\rightleftharpoons$ trans-allylic isomerizations of radicals must surmount a large energy barrier,[18] the cis-allylic configuration would be required at the birth of the diradical in order to form the bicyclo[3.2.2]nonadiene product **20a**. Direct ring closure of the trans-allylic species **33** would lead to a highly strained bicyclo[3.2.2]nonadiene product with a trans double bond. However, cyclization of the trans-allylic radicals **32** and **33** to either of the cyclopropane intermediates **28** or **29** would encounter no such problem. If the diradical mechanism for formation of **29** is correct, the diradical intermediate would be formulated more plausibly as **33** than as **27**.

Not only the *endo*-7-propenyl compound **29** but also its exo isomer **28** could serve as intermediates. Compound **28** (Scheme III) could be formed from **1** or **2** either by cyclization of a diradical **33** as described above or in concerted processes (a "forbidden" retention reaction from **1** and an "allowed" inversion one from **2**). The conversion of **28** to **20a** would require an overall stereodistal Cope rearrangement.[19] Although a direct process **28** → **20a** cannot yet be ruled out, analogy to the case of *trans*-1,2-dialkenylcyclobutanes,[19a] where an indirect stepwise mechanism involving prior epimerization to a *cis*-1,2-dialkenylcyclobutane prevails, suggests that the preliminary epimerization of **28** to **29** followed by a boat-like Cope rearrangement is a more likely alternative. Regardless of whether the direct or indirect mechanism is correct, the stereochemical outcome would be the same and would lead to the observed product, **20a**. The overall stereochemistry has a very close analogy in the rearrangements of *trans*-1,2-dialkenylcyclopropanes,[19b] which give products from boat-like stereodistal Cope processes with high stereospecificity.

Rearrangement by a mechanism analogous to that of Scheme III might be expected to lead to a different result when applied to the syn-cis substrate **3**. By analogy to the model compound **34**, which undergoes



34 **35**

Cope rearrangement stereospecifically (again in the boat geometry) but only under forcing conditions,[16b] the intermediate *cis*-propenyl compound **35** which would be formed from syn-cis substrate **3** should rearrange much more slowly than its trans-propenyl isomer **29**. With the exit step from **35** to the ultimate bicyclo[3.2.2]-nonadiene ring system thus severely retarded, it would not be surprising if the pyrolysis of the syn-cis substrate **3** employed a mechanism partly or completely by-passing intermediate **35**, perhaps by way of direct closure of a diradical intermediate or by competing allowed and forbidden concerted pathways. If a *syn*-divinylcyclopropane were no longer an obligatory intermediate, we should expect a marked diminution in the stereospecificity of the overall rearrangement, since no other pathways seem to require high stereospecificity. This is consistent with the observation (Table II) that the stereospecificity falls from >99:1 in the cases of *trans*-propenyl substrates **1** and **2** to only about 2:1 in the case of *cis*-propenyl substrate **3**.

We conclude that the most plausible mechanism for the rearrangements of **1** and **2** is that shown in Scheme III, namely a [1,3]-sigmatropic shift of (unknown concert) to produce an intermediate *exo*- or *endo*-7-propenylbicyclo[4.1.0]heptene (**28** or **29**) followed by ordinary Cope rearrangement of the endo compound **29** and stereodistal Cope rearrangement of the exo isomer **28**. If this is correct, the long-sought thermal antarafacial-retention [1,3]-sigmatropic rearrangement, even in a system designed to force retention of configuration on the migrating group, once more has eluded detection.[20]

Experimental Section[22]

Infrared spectra (maxima reported in cm^{-1} or μ, as indicated) were recorded on a Perkin-Elmer 337 spectrophotometer using chloroform as solvent except as indicated. The nmr spectra (chemical shifts in δ units relative to tetramethylsilane) were run using Varian Associates A-60A or Jeolco JNM-MH-100 spectrometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparative gas–liquid partition chromatography (vpc) separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with a thermal conductivity detector and used helium as the carrier gas. Analytical vpc determinations were performed using a Perkin-Elmer Model 900 gas chromatograph equipped with

(18) *Cf.* R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Amer. Chem. Soc.*, **93**, 3810 (1971).

(19) (a) J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **94**, 8949 (1972), and references cited therein; (b) C. Ullenius, P. W. Ford, and J. E. Baldwin, *ibid.*, **94**, 5910 (1972).

(20) The antarafacial process that is reported[21] to occur in the rearrangements of methylenecyclobutanes starts with the migrating carbon *in the π-nodal plane* of the migration framework. It seems reasonable to consider such reactions in a separate category, since they require much less severe uncoupling of orbitals than those required for antarafacial migration in the present systems. In fact, in the methylenecyclobutane cases, the relative motions of the migrating group and the migration terminus in the antarafacial–retention and suprafacial–retention pathways are stereochemically indistinguishable. The two processes differ only in the relative torsional motion of the migration origin.

(21) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **94**, 2140 (1972).

(22) We acknowledge with thanks the technical assistance of Messrs. Joseph Sandrowski, Corning Lahey, and John Kotuby in the preparation of some of the starting materials.

a flame ionization detector and a capillary column and used nitrogen as the carrier gas. The column descriptions are as follows.

Column designation	Description	Stationary phase
A	10 ft × 0.375 in.	23% Carbowax 20M on 60–80 Chromosorb W (No. 15)
B	20 ft × 0.375 in.	20% FFAP on 60–80 Chromosorb W (No. 33)
C	224 ft capillary (0.01 in. i.d.)	TCEP

Reaction of Norborn-2-en-7-one with the Lithium Reagent from 1-Bromo-1-propene and Subsequent Etherification. Lithium reagent was prepared by the addition of 6 ml of 1-bromo-1-propene (Aldrich) to a mixture of 0.65 g (92.0 mg-atom, 15 cm wire) of lithium chunks in 50 ml of dry tetrahydrofuran (THF) under nitrogen at 0°. Iodine facilitated the onset of reaction, and in *ca.* 2 hr the lithium metal had been consumed with the formation of a white precipitate. To this stirred mixture was added 2.99 g (27.7 mmol) of norbornen-7-one[23] in 10 ml of dry THF. After 18 hr the mixture was treated with 100 ml of water followed by ether extraction (2 × 100 ml). Evaporation *in vacuo* of the dried ($MgSO_4$) organic portion gave a clear oil (3.10 g) which was used in the etherification procedure with Na–K alloy and MeI (*vide infra*). Vpc analysis of the product (column A, 160°, 80 ml/min) indicated a complex mixture quite different in composition from that obtained *via* the Grignard reagent procedure. Besides several short retention time peaks, the product consisted of three materials in a ratio 1:5:4 at relative retention times, 17.8, 23.5, and 27.4 min.

Careful separation on a preparative scale gave the following fractions: fraction 1, retention time 17.8 min, identified by comparison with an authentic sample (see below) as mostly *anti*-7-*trans*-propenyl-*syn*-7-methoxynorborn-2-ene (**2**); fraction 2, retention time 23.5 min, *syn*-7-propynyl-*anti*-7-methoxynorborn-2-ene (**7**) (this substance showed the spectroscopic properties given in Table I); fraction 3, retention time 27.4 min, *anti*-7-propynyl-*syn*-7-methoxynorborn-2-ene (**8**). The nmr and ir spectra are given in Table I.

The effects of incremental amounts of $Eu(fod)_3$ on the nmr spectra of compounds **7** and **8** are listed in Table III.

Table III. Effect of $Eu(fod)_3$ on the Nmr Spectra of Compounds **7** and **8**

Compd	Mole ratio $Eu(fod)_3$/compd	Δδ, Hz $H_3(a)$	$H_3(b)$	CH_3	H_1	OMe	H_2
7	0	0	0	0	0	0	0
	0.3	0	8	0	5	10	3
	0.435		22	7	21	21	10
	0.715	21	50	18	52	55	23
8	0.18	9	2	2	22	19	17
	0.685	52	57	25	127	120	118

syn-7-*trans*-**Propenyl**-*anti*-7-**methoxynorbornene (1).** A 100-ml three-necked flask cooled in a Dry Ice–acetone bath and fitted with a Dry Ice condenser was charged under nitrogen with 20 ml of liquid ammonia from a lecture bottle. With the addition of 200 mg (8.7 mg-atoms) of sodium chunks, a dark blue color developed and the metal was consumed. *syn*-7-Propynyl-*anti*-7-methoxynorborn-2-ene (**7**) (430 mg, 2.65 mmol) was added *via* syringe, and the mixture was stirred under reflux for 2 hr. Addition of ammonium nitrate solid, followed by 50 ml of water, gave a clear aqueous layer which was extracted with ether (2 × 50 ml). Evaporation *in vacuo* of the dried ($MgSO_4$) organic portion gave a clear oil which was purified on column A. Capillary vpc analysis (column C, 85°) showed the product to be 99.6% of **1** and 0.4% of **3**. The nmr and ir spectra are given in Table I. Consistent with the assignment of trans stereochemistry about the propenyl group, spin decoupling experiments (100 MHz) revealed the following coupling constants: propenyl HC=CH, 12 Hz; propenyl Me-*gem* =CH, 6 Hz; propenyl Me-*vicinal* =CH, 0 Hz.

(23) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.76. Found: C, 80.20; H, 9.84.

anti-7-*trans*-**Propenyl**-*syn*-7-**methoxynorbornene (2).** The above procedure was carried out using 582 mg (3.59 mmol) of *anti*-7-propynyl-*syn*-7-methoxynorborn-2-ene (**8**), 800 mg (34.8 mg-atoms) of sodium metal, and 40 ml of liquid ammonia. Analysis of the crude product (column C, 115°, retention time 12.0 min) again showed largely a single component which was identical with the minor ether product derived *via* the lithium reagent procedure. Purification by vpc on column A and analysis on column C gave material consisting of 97.3% of **2** and 2.7% of two impurities, neither of which was **1** or **3**.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.76. Found: C, 80.46; H, 9.80.

syn-7-*cis*-**Propenyl**-*anti*-7-**methoxynorbornene (3). Grignard Addition to Norbornenone and Subsequent Etherification.** To a Grignard solution prepared from 24 ml of 1-bromo-1-propene and 6 g (250 mg-atom) of magnesium turnings in 100 ml of dry THF, a solution of 9.5 g (88 mmol) of norborn-2-en-7-one was added dropwise at room temperature. After the mixture was stirred for 5 hr, work-up was accomplished by the addition of 600 ml of water and 100 ml of 1 *N* HCl and extraction with ether. The dried ether ($MgSO_4$) was evaporated to give 13.2 g of a yellow oil which was distilled to give 12.8 g of a mixture of alcohols, bp 100–125° (20 mm). Sodium–potassium alloy was prepared by warming the metals (3 g of Na and 6 g of K) gently with a flame under nitrogen atmosphere. The resulting paste was covered with 100 ml of dry ether. A solution of the alcohols in 40 ml of ether was added with vigorous stirring. The stirring was continued until no more hydrogen evolved (*ca.* 3 hr). Then 40 ml of methyl iodide was added in one portion, and stirring was continued for 12 hr at room temperature, 100 ml of methanol was added carefully to decompose the excess alloy, and the resulting mixture was poured into 500 ml of water. Extraction followed by evaporation gave 9.7 g of a yellow oil which was distilled to give 9.4 g of a colorless oil, bp 92–105° (8 mm).

Vpc analysis column A revealed that the product consisted mainly of four materials in a ratio 6:2:1:1 approximately. Separation was carried out at 190° and a flow rate of 100 ml/min. The collected fractions were purified on the same column (at 170°, 100 ml/min) to give the following fractions: fraction 1, 5.8 g; vpc analysis on column C at 85° showed this fraction to be 75% of **3** (retention time 12.76 min) and 25% of **1** (retention time 13.84 min); fraction 2, 1.3 g, vpc analysis on column C showed this fraction to be 39% of an unidentified component (7-*anti*, *cis*-propenyl?) (retention time 24.52 min) and 61% of **2** (retention time 28.10 min); fraction 3, 0.6 g, acetylenic ether (**7**); fraction 4, 0.3 g, acetylenic ether (**8**).

The mixture of **3** and **1** (1 g) which was obtained as fraction 1 in the above Grignard reaction was sealed into a Carius tube (volume 40 cm^3) at 0.3 mm. After 75 min heating at 289.5° in a salt bath, the resulting pyrolysate was dissolved in 10 ml of $CHCl_3$ and the solution was boiled under reflux for 1 day. The material from five such runs, after evaporation of $CHCl_3$, was distilled at 8 mm to give the following four fractions: fraction 1, 560 mg, bp 95–100°; fraction 2, 420 mg, bp 100–105°; fraction 3, 1.60 g, bp 105–110°; fraction 4, 2.2 g, bp 110–125°. Vpc analysis revealed that most of the recovered starting material was concentrated in fractions 1 and 2, whereas fractions 3 and 4 were mostly composed of rearrangement products. From the fractions 1 and 2, 780 mg of crude **3** was collected (column A, 165°). A pure sample of **3** was obtained by purification on the same column at 155°. This material was composed of 99.3% of **3** and 0.7% of three other impurities, none of which was **1**. The nmr and ir spectra are given in Table I.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.76. Found: C, 80.49; H, 9.82.

4-Methylbicyclo[3.2.2]nona-6,8-dien-2-one (22).[9] To a stirred mixture of 50 mg (0.5 mmol, 5 mol %) of cuprous chloride and 0.38 g (16.0 mg-atoms) of magnesium turnings in 80 ml of anhydrous ether was added 6.5 ml (2.85 g, 20.0 mmol) of methyl iodide in two portions. The cloudy mixture was stirred until the magnesium had been consumed (*ca.* 2 hr). A solution of bicyclo[3.2.2]-nona-2,6,8-trien-4-one (**21**)[8] (1.40 g, 10.6 mmol, crude product from chromatography) in 20 ml of ether was added dropwise, and the resulting mixture was allowed to stir for 18 hr. Work-up proceeded with the addition of 100 ml of 5% hydrochloric acid (to prevent emulsion) and extraction with ether (2 × 100 ml). The dried ether extracts provided 1.44 g of a brown oil which was chromatographed on a 5 × 28 cm column of silica gel, slurry packed in 20% ether–hexane. The following 2-l. fractions were taken: (1) 20% ether–hexane, 0.937 g (60%), desired dienone; (2) 50% ether–hexane,

0.345 g (22%), mostly 4-methylbicyclo[3.2.2]nona-2,6,8-trien-4-ol (mixture tentatively identified by nmr).

Although the products from chromatography were accompanied by a small amount of tarry material, the dienone fraction was found suitable for use in the next step. A sample was purified by vpc (column A, 190°, 80 ml/min, retention time 25.8 min). The spectral data were: ir ($CHCl_3$) 3.42, 5.95, 8.80, 11.10, and 11.80 μ; nmr (CCl_4) δ 0.98 (d, J = 6 Hz, 3 H, CH_3), 1.90–2.50 (m, 3 H, aliphatic), 2.80–3.20 (m, 1 H, bridgehead CH), 3.40–3.75 (m, 1 H, bridgehead α to carbonyl), and 5.90–6.60 (m, 4 H, olefinic).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 81.06; H, 8.20.

Catalytic Hydrogenation of 4-Methylbicyclo[3.2.2]nona-6,8-dien-2-one (22). Atmospheric hydrogenation of the dienone fraction from chromatography in the presence of 10% Pd/C failed in a number of solvent systems. On the other hand, the theoretical quantity (1 molar equiv) of hydrogen was consumed in 10.5 hr when the dienone (1.00 g, 6.70 mmol) was routinely hydrogenated (1 atm, room temperature) in 30 ml of absolute ethanol in the presence of platinum oxide (83.54%, Engelhard Industries, Inc.). Capillary vpc analysis (column C, 120°) of the product revealed four components in the ratios 2:4:1:2, with relative retention times 42.57, 51.88, 55.00, and 56.14 min, respectively, the first and fourth of which were identified as the epimeric ketones isolated from the pyrolysis (see below) of the 7-methoxy-7-propenyl-2-norbornenes. This mixture could not be resolved by vpc using a wide variety of packed columns or by conventional chromatography on silica gel or Florisil.

Chromatography of the hydrogenation mixture on a 3.5 × 40 cm column of 20% silver nitrate–silica gel (prepared by mixing 100 g of silver nitrate, 400 g of silica gel, and 500 ml of water, removal of water *in vacuo*, and drying solid at 120° for 24 hr), slurry packed in 20% ether–hexane gave the following fractions: (1) 1000 ml, 10% ether–hexane, 0.390 g, 4-methylbicyclo[3.2.2]octan-2-one; nmr (CCl_4) δ 1.00 (d, J = 6 Hz, 3 H, CH_3), 1.40–2.10 (m, 10 H, aliphatic), and 2.10–2.45 (m, 3 H, aliphatic); (2) 500 ml, 20% ether–hexane, 0.290 g, *endo*-methyl ketone **20a** contaminated with the fully saturated ketone; (3) 500 ml, 20% ether–hexane, 0.196 g, *exo*-methyl ketone **20b**; (4) 1000 ml, 20% ether–hexane, 0.141 g, **20b** plus an unidentified material; and (5) 1000 ml, 50% ether–hexane, 0.249 g, mostly starting dienone.

Pure samples of the desired monohydrogenated products **20a** and **20b** were obtained by preparative vpc (column A, 180°, 80 ml/min) of the appropriately enriched column chromatographic fractions (column separation was not optimized). Comparison of spectral data (ir, nmr) of the epimeric ketones derived synthetically showed them to have properties identical with those of the pyrolysis products.

***endo*-4-Methylbicyclo[3.2.2]non-6-en-2-one (20a)** showed prominent ir bands at 3.45, 5.95, 6.85, and 8.25 μ; nmr (CCl_4) δ 1.00 (d, 3 H, J = 6 Hz, CH_3), 1.50–2.70 (m, 8 H, aliphatic), 2.75–3.15 (m, 1 H, bridgehead, CH α to CO), and 6.20 (d × d, J = 2 and 5 Hz, olefinic).

Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.77; H, 9.43.

***exo*-4-Methylbicyclo[3.2.2]non-6-en-2-one (20b)** showed prominent ir bands at 3.45, 5.95, 6.80, 8.25, 11.00, and 11.30 μ; nmr (CCl_4) δ 1.00 (d, J = 6 Hz, 3 H, CH_3), 1.40–2.70 (m, 8 H, aliphatic), 2.80–3.10 (m, 1 H, bridgehead CH α to CO), and 5.80–6.60 (symmetrical six-line pattern, 2 H, olefinic).

Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.91; H, 9.36.

Synthesis of 20a and 20b (Scheme I). Hydrocyanation of 21. A solution of 28 g of material obtained from the preparation of **21**[8] (consisting of 75% of **21** and 25% of 1-indanone) (0.159 mol), 19 g of KCN (0.29 mol), 12 g of NH_4Cl (0.24 mol) in 600 ml of dimethylformamide (DMF), and 80 ml of water was heated at 100° under nitrogen for 12 hr. Concentration of DMF *in vacuo*, dilution with water, and extraction with ether gave 23 g of a dark brown oil which crystallized. Addition of cold ether followed by filtration gave 13 g of pale yellow crystals, mp 95–96°. Recrystallization from hexane–ether gave 12.2 g (48.3%) of 4-cyanobicyclo[3.2.2]-nona-6,8-dien-2-one as colorless needles: ir (Nujol) 1701 cm^{-1}; nmr ($CDCl_3$) δ 6.67–6.30 (4 H) and 2.65–4.0 (5 H).

Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.51; H, 5.72; N, 8.79.

4-Carboxybicyclo[3.2.2]nona-6,8-dien-2-one. A solution of 1.8 g (11 mmol) of the above cyano ketone in 24 ml of 1 *N* NaOH and 96 ml of methanol was refluxed for 24 hr under nitrogen. After evaporation of methanol followed by dilution with water, the aqueous alkaline solution was extracted with ether to remove a neutral material. Then the alkaline layer was acidified with 6 *N* HCl and extracted with $CHCl_3$. After washing with water and drying over $MgSO_4$, chloroform was evaporated to give 1.4 g of a brown oil as an acidic product. Addition of a small amount of ether followed by cooling gave 690 mg (30%) colorless crystals, mp 116–117°. Recrystallization from hexane–ether gave colorless prisms, mp 119–120° of 4-carboxybicyclo[3.2.2]nona-6,8-dien-2-one: ir (Nujol) ~3100, 1735, 1670 cm^{-1}; nmr ($CDCl_3$) 6.40 (m, 4 H), 4.0–2.30 ppm (6 H). Analysis showed this material to be slightly impure.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 66.24, 66.31; H, 5.96, 5.91.

***endo*-4-Carboxybicyclo[3.2.2]non-6-en-2-one.** A sample of 100 mg (0.56 mmol) of the above dienone acid was reduced in 15 ml of methanol in the presence of a catalytic amount of prereduced 10% Pd/C. After 11 ml of hydrogen was absorbed, the catalyst was filtered off and the methanol was evaporated to give 100 mg of a clear oil. Nmr analysis showed ratio of methine and methylene protons to vinyl protons to be 5:1.

To a vigorously stirred solution of 300 mg (1.7 mmol) of this material pooled from several runs and 300 mg of sodium carbonate in 20 ml of water, 0.2 ml of bromine was added dropwise at room temperature. Stirring was continued for 15 min. The solution turned yellow and a precipitate appeared. After the addition of a small amount of sodium sulfite, the resulting solution was extracted with $CHCl_3$, and the $CHCl_3$ extract was washed with water and dried over Na_2SO_4. Evaporation of chloroform gave 140 mg (32%) of bromolactone **23** as a viscous oil. This material was used for the next step without purification: ir (neat) 1775 and 1710 cm^{-1}; nmr ($CDCl_3$) 4.20 (broad doublet, 1 H, J = 3.5 Hz); 5.05 (quartet, 1 H, J = 1.5 and 8.0 Hz); 2.10 (m, 4 H), 2.30–3.60 (m, 5 H).

A sample of 90 mg (0.35 mmol) of **23** and 0.4 g of Zn dust was refluxed in 30 ml of ethanol for 4 hr. After filtration, the ethanol was concentrated to give 81 mg of a viscous oil which was treated with 10 ml of 1 *N* HCl for 1 hr. After extraction with $CHCl_3$, the chloroform solution was washed with water and then dried over $MgSO_4$. Evaporation of chloroform gave 68 mg of a viscous oil which crystallized on standing. Recrystallization from hexane–ether gave 55 mg of endo acid as colorless prisms, mp 108–109°. This acid gave bromolactone **23** in 79% yield in the same treatment as before: ir(Nujol) 1700 cm^{-1} (broad) and ~3100 cm^{-1}; nmr ($CDCl_3$) 6.33 (m, 2 H); 1.87 (m, 2 H); 2.44–4.00 ppm (m, 8 H).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.38; H, 6.65.

Ethylene Ketal of *endo*-4-Carboethoxybicyclo[3.2.2]non-6-en-2-one. A 1.3-g sample of the above acid was esterified with diazoethane in ether to give 1.28 g (86%) of the corresponding ethyl ester, bp 125–130° (0.2 mm). A solution of 1.2 g (5.8 mmol) of this material and 30 mg of *p*-toluenesulfonic acid in 50 ml of ethylene glycol was heated for 2 hr at 80–85°. Then ethylene glycol was distilled *in vacuo* at this temperature over a period of 4 hr. The residue was dissolved in chloroform, and the solution was washed with water and dried over Na_2SO_4–K_2CO_3. Evaporation of the dried chloroform gave 940 mg of a dark oil which upon distillation (bp 140–150° (0.2 mm)) gave 710 mg (49%) of the ketal ester as a colorless oil: ir (neat) 1735 cm^{-1}; nmr ($CDCl_3$) 6.25 (m, 2 H); 3.95 (broad singlet, 4 H); 1.50–3.00 (m, 9 H); 1.25 (t) and 4.15 (q, ethyl).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 67.17, 67.22; H, 7.60, 7.57.

***endo*-4-Methylbicyclo[3.2.2]non-6-en-2-one (20a).** To a solution of 190 mg (5.0 mmol) of $LiAlH_4$ in 15 ml of dry ether, a solution of 700 mg (2.8 mmol) of the endo-ketal ester in 30 ml of ether was added. This solution was stirred for 8 hr and then heated at reflux for 1 hr. After addition of 20 ml of 1 *N* HCl, the resulting mixture was stirred for 12 hr at room temperature. The ether layer was separated and the aqueous layer was extracted with ether. Evaporation of the dried ether (magnesium sulfate) gave 380 mg (80%) of keto alcohol as a pale yellow oil which was used for the next step without purification: ir (neat) 3400 and 1700 cm^{-1}, nmr 6.15 (m, 2 H); 1.78 (broad singlet, 2 H); 3.60–2.00 (m, 10 H).

To a cold solution of 380 mg (2.3 mmol) of this material in 2 ml of pyridine, 870 mg (4.6 mmol), of *p*-toluenesulfonyl chloride was added. The resulting pale yellow solution was kept in the refrigerator for 24 hr, then poured into ice–water, and extracted with ether. The extract was washed with 6 *N* HCl and water. Evaporation at room temperature of the dried ether (Na_2SO_4–K_2CO_3) gave 330 mg (45%) of toluenesulfonate as a brown oily material: ir (neat) 1700, 1340, and 1175 cm^{-1}.

To a solution of 150 mg (0.47 mmol) of the toluenesulfonate in 15 ml of ether, 25 mg (0.66 mmol) of $LiAlH_4$ was added and the solution was stirred for 18 hr at room temperature and then boiled at reflux for 2 hr. Treatment with 1 *N* HCl, extraction with ether, and evaporation of the dried ether ($MgSO_4$) gave 49 mg (68.5%) of a clear pale yellow oil. Vpc analysis (capillary TCEP, 115°) showed 91% of this consisted of two alcohols in the ratio of 1.7:1. These alcohols were identical with two alcohols which were obtained from $LiAlH_4$ reduction of **20a** by ir, nmr, and vpc analysis: ir (neat) 3350, 1460, 1380, and 1265 cm^{-1}, nmr ($CDCl_3$) 6.10 (m, 2 H); 1.17 (m, 3 H, methyl), 0.75–4.0 (m, 11 H).

To a solution of 72 mg (0.47 mmol) of the mixed alcohols in 2 ml of acetone, Jones reagent was added at 0° until a solution turned to pale yellow. After dilution with water the solution extracted with ether. Evaporation of the dried ether gave 51 mg (72%) of **20a**, identical with the pyrolysis product from **1** and **2** as judged by ir (neat), nmr, and vpc analysis (column C).

***exo*-4-Methylbicyclo[3.2.2]non-6-en-2-one (20b).** To a sample of the ethylene ketal of *endo*-4-carboethoxybicyclo[3.2.2]non-6-en-2-one (53 mg) in 1 ml of ethanol, a solution of NaOEt (trace) in 1 ml of ethanol was added. The resulting reddish brown solution was kept in the refrigerator for 2 days, then poured into ice–water and extracted with ether. The ether extract was washed with water and dried over Na_2SO_4. Evaporation of the ether gave 47 mg (89%) of an epimerized mixture as a pale yellow oil: ir (neat) 1735 cm^{-1}; nmr ($CDCl_3$) 6.15–6.55 ppm.

This material and 15 mg of $LiAlH_4$ in 15 ml of ether (0.4 mmol) of $LiAlH_4$ were stirred for 4 hr and then heated at reflux for 1 hr. After addition of 10 ml of 1 *N* HCl, the resulting mixture was stirred for 16 hr at room temperature. Extraction with ether followed by washing and evaporation gave 27 mg (85%) of keto alcohol mixture.

A solution of 27 mg (0.16 mmol) of the keto alcohol mixture and 60 mg (0.32 mmol) of *p*-toluenesulfonyl chloride in 1 ml of pyridine was kept in the refrigerator for 23 hr. The same treatment as before gave 19.5 mg (38%) of a mixture of tosylates. This was mixed with 10 mg (0.3 mmol) of $LiAlH_4$ in 5 ml of ether and stirred for 24 hr. The same treatment as before gave 7.0 mg (75%) of an alcohol mixture as a clear oil. Vpc analysis (column C, 115°) revealed that this mixture was composed of three alcohols in amounts of 19.8, 33.0, and 47.2%. These three alcohols had retention times identical with those of the alcohols obtained from $LiAlH_4$ reduction of the pyrolysis products, **20a** and **20b**.

The alcohol mixture was treated with Jones reagent in 1 ml of acetone to give a ketone mixture composed of 42.7% of **20a** and 57.3% of **20b** as demonstrated by comparison of vpc retention times (on column C at 115°) with those of the pyrolysis product ketones.

Pyrolyses of 1, 2, and 3 were carried out using samples which were purified by vpc, weighed into 4 × 130 mm Pyrex tubes, and placed in Carius tubes of 10 or 40 ml volume. The tubes were deoxygenated by repeated cycles of evacuation and filling with nitrogen, sealed, and placed in a molten salt bath at the indicated temperature. The temperature was controlled by a Bayley proportional controller to ±0.1° and measured by a calibrated thermocouple. The reported temperatures probably are accurate to ±0.1°. After being cooled to ice bath temperature and then to −78°, each tube was opened and treated with 0.5 ml of $CHCl_3$ and 10 μl as internal standard, resealed, and allowed to stand at room temperature for 5 days in the dark. Analysis by capillary vpc was carried out with column C. The distributions of products are given in Table II. The rate constants shown in Scheme II were obtained by multiplying the first-order rate constant for overall decomposition of the starting material (relative to an internal standard) by the fraction of the indicated product formed. Plots of log (per cent starting material unreacted) *vs.* time were linear during 1–3 half-lives, but the rate constants probably are accurate only to about ±20%.

Control experiments showed that the product compositions did not vary as a function of the per cent conversion of starting material (**1** or **2**) within a run. Both the rates and product distributions were also invariant to a twofold change in surface to volume ratio.

Runs on a preparative scale used several tenths of a gram of starting material and were carried out in sealed 150 ml Pyrex Carius tubes which previously had been successively washed with cleaning solution, water, ammonia, and water. Separation of the products by vpc on column A at 180° was based upon retention times of 23.2 and 25.2 min for the two bicyclo[4.3.0]nonenones **19a** and **19b**, and of 28.0 and 32.5 min for *endo*- and *exo*-4-methylbicyclo[3.2.2]-non-6-en-2-one, **20a** and **20b**, respectively.

A mixture of 9-methylbicyclo[4.3.0]non-2-en-7-ones, **19a** and **19b** obtained as a difficultly separable mixture, showed ir bands at 3.45, 5.80, and 8.85 μ. The nmr showed absorptions at δ 1.15 (d, 3 H, J = 6 Hz), 1.60–3.00 (m, 9 H), and 5.72 (broad s, 2 H). Separation of small amounts by vpc for microanalysis gave a not quite pure sample of **19a** and analytically pure **19b**. *Anal.* Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. *Found* (for **19a**): C, 78.83; 78.76; H, 9.16, 9.21. *Found* (for **19b**): C, 79.75; H, 9.44.