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THE STEREOCHEMISTRY AND MECHANISM OF THE [σ2 + σ2 + σ2] CYCLOREVERSION[a]

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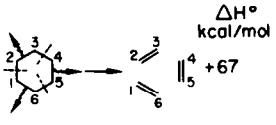
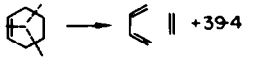
Abstract—The search for concert in the cycloreversion of a 6-membered ring to three pi-bonded fragments uses three mechanistic criteria: an enhanced rate as compared to model compounds, the absence of ring-closure products, and stereospecificity. By these criteria, the decompositions of 1,2-diazacyclohexa-1,4-dienes (**57**) and 2,3-diazabicyclo [4.1.0] hept-2-enes (**58**) are clearly concerted. The decomposition of 2,3-diazabicyclo [4.2.0] oct-2-enes (**59**), although it shows only a small rate enhancement, nevertheless meets the product and stereospecificity criteria and probably is concerted. The data suggest that the degree of concert gradually declines as the pi-character of the participating ring bond decreases. The cycloreversions of both sets of bicyclic compounds **58** and **59** follow an "inward-disrotatory" path undoubtedly because their transition states have the most efficient orbital overlap. An analysis of the [2 + 2 + 2] cycloreversion reveals an ambiguity in nomenclature that is a general feature of the Woodward-Hoffmann Rules in their 2-electron-component form. For a reaction involving any given number of such components, all allowed stereochemical pathways have the same set of descriptions.

Sigma bonds are less polarizable than pi bonds and therefore might be expected to participate less readily in a concerted, thermal, electrocyclic reaction, where the bonds are extensively delocalized in the transition state. There are several concerted reactions in which both pi and sigma bonds participate, but relatively few all-sigma processes.

As a particularly stringent test of sigma participation, we seek to devise and identify thermal reactions in which simultaneous rupture of three (C_1–C_2, C_3–C_4, C_5–C_6) of the six sigma bonds of a 6-membered ring gives three pi-bonded fragments. In this process, the original C_2–C_3, C_4–C_5, and C_6–C_1 sigma bonds remain intact. The simplest conceptualization of such an event would be an "explosion" of a cyclohexane ring to yield three molecules of ethylene (Eq 1). Beyond mere whimsey, the analogy to an actual physical explosion is useful, because it focuses attention on two characteristic features of the model, the large exothermicity and the transformation of some of the released energy to kinetic energy of the fragments. Both of these features are relevant to a realization of the chemical reaction.



(1)



(2)

The test is loosely defined, of course. Thus, the term "participate" implies that in the transition state, a bond ultimately to be broken already is weakened. However, one could imagine such weakening in the case of bonds that survive an individual step or even the overall reaction. Moreover, the terms "simultaneous" and "concerted" are notoriously imprecise, since they ignore presently difficult or intractable problems, such as chemical activation effects, flat regions or other pecularities of reaction energy surfaces, dynamic effects, and others. These shortcomings, however, apply to all studies of mechanism. Therefore, we press on in an attempt to gain some experimental information that might be mechanistically interpretable, or at least, might help in the formulation of more precise questions.

Thermochemistry and thermodynamics of reactions related to the fragmentation of cyclohexane

Our understanding of the details of energy distribution in unimolecular fragmentation reactions is still very primitive, but chemical intuition would suggest that unless the cyclohexane decomposition of Eq 1 were strongly exothermic, or more properly, exergonic, it would not occur.

From standard thermodynamic data,[1] it can be calculated that the reaction of Eq 1 has the values

[a] Part of this work is taken from the Ph.D. Dissertation of Edward W. Petrillo, Jr., Yale University, 1973. Preliminary communications: Refs 15, 24, and 32.

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$\Delta H° = +67$ kcal/mole, $\Delta S° = +85{\cdot}9$ gibbs/mole at 25°C. The severe endothermicity is offset to some extent by the favorable $-T\Delta S°$ effect,* but the reaction is still discouragingly endergonic: $\Delta F° = +41{\cdot}2$ kcal/mole. Clearly, it will be necessary to modify the idealized process of Eq 1.

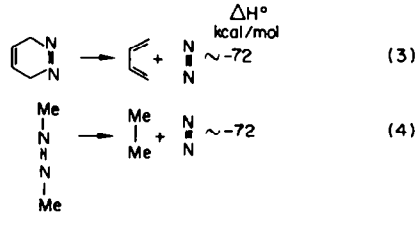
One form that such a compromise might take would be to replace one or more of the cyclohexane sigma bonds by weaker bonds, thereby decreasing the endothermicity. For example, the retro-Diels-Alder decomposition of cyclohexene to butadiene and ethylene (Eq 2), has $\Delta H° = +39{\cdot}4$ kcal/mole. Replacement of one of the sigma bonds by a pi bond thus makes the reaction less endothermic by about 26 kcal/mole. However, the whole benefit of this replacement cannot be realized. Primarily because the decomposition now gives only two fragments instead of three, the favorable entropy effect is much smaller ($\Delta S° = +46{\cdot}1$ gibbs/mole), and the reaction is still endergonic: $\Delta F° = +25{\cdot}2$ kcal/mole.

Of course, this pi-for-sigma substitution dilutes some of the significance of the proposed experiments, since the participation of a relatively weak, easily deformed pi bond puts less stringent requirements on concert than would be the case with a sigma bond. However, as will become clear, this is only a temporary device, and in due course, sigma character will be restored to the bond in question.

Further modifications of the basic system of Eq 2 might include the incorporation of ring-strain in the cyclohexene. For example, the strain energy of norbornene (20 ± 3 kcal/mole[1]) should permit a concerted Diels–Alder cycloreversion to cyclopentadiene and an olefin, in agreement with observation.[2]

For our purposes, however, it is necessary to retain the 6-membered ring in unbridged form, so as to permit stereochemical observations. Therefore, improvement of the thermodynamic driving force must be achieved by weakening the remaining target sigma bonds. This amounts to using a better retro-Diels–Alder "leaving group" (a weaker dienophile). In this way, we are led to consider the 1,2-diazacyclohexa-1,4-diene system (Eq 3).

The decomposition of azomethane to ethane and nitrogen (Eq 4) serves as a model for the calculation of the thermochemistry of Eq 3. Eq 4 has $\Delta H° = -72$ kcal/mole ($\Delta H_f°$ of azomethane $= +52$ kcal/mole[3], $\Delta H_f°$ of ethane $= -20{\cdot}2$ kcal/mole[1]). There are only two significant thermochemical differences between Eq 3 and Eq 4 (aside from small corrections for hybridization). Eq 4 is made more exothermic by roughly the difference in strength between a C–C pi bond and a C–C sigma bond, and it is made less exothermic by the difference in strength between two allylic and two non-allylic C–N sigma bonds. Although there are some questions about the exact values of these increments,[4-6] they are not far out of balance, so that the decomposition of 1,2-diazacyclohexa-1,4-diene (Eq 3) must be exothermic about the same amount as Eq 4. This is a healthy improvement of some 139 kcal/mole in exothermicity as compared to Eq 1!



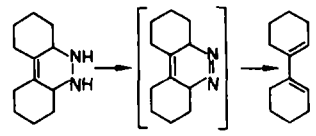
*In the reverse of Eq 1, *i.e.*, in the hypothetical concerted, homogeneous, termolecular combination to give cyclohexane, most of the entropy of three ethylenes would be lost in the transition state, so that the $-T\Delta S°$ contribution to $\Delta F°$ would be close to the overall $-T\Delta S°$, about +26 kcal/mole.

Cycloreversions of 1,2-diazacyclohexa-1,4-dienes

With the structural elements needed for an exothermic reaction now having been identified, we can proceed to test the cycloreversions of 1,2-diazacyclohexa-1,4-dienes for participation of the C–C pi bond. The three criteria that seem applicable are a rate of decomposition much faster than that of saturated models, the absence of ring-closure products, and stereospecificity.

The first criterion derives from the assumption that the energy cost of the partially broken pi bond in the transition state would be more than repaid in the energy benefit of two partially formed new pi bonds. The second criterion is really a corollary of the first. It assumes that a transition state with a partially broken pi bond would go on to a product with that bond fully broken. The third criterion assumes that a strongly concerted reaction usually would use some pathway with a high stereoelectronic preference, for reasons of orbital overlap or orbital symmetry. The criteria are not strict, and it is easily possible to imagine circumstances in which a concerted process would violate one or more of them. However, they do define a pattern of idealized behavior for comparison with experimental results. There have been relatively few cases in which it has been possible to apply all three criteria, but the evidence in the case of the diazacyclohexadienes is now reasonably complete.

It comes as no surprise that reactions with the thermodynamic driving force of Eq 3 are rapid. For example, Gillis and Beck[7] report that the diene **3** is the only observed product of the oxidation of the olefinic hydrazo compound **1**. Presumably the intermediate azo compound **2** decomposes too rapidly to permit isolation. Similarly, Askani[8] and Lemal *et al.*[9] find that 2,3-diazabicyclo [2.2.2] octa-2,5-diene **5**, presumably formed in the oxidation of the hydrazo compound **4**, decomposes to cyclohexa-1,3-diene and nitrogen even at −78°.



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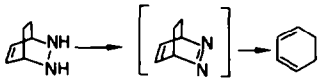
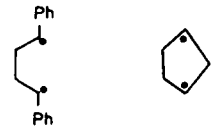


4 5

These unsaturated azo compounds decompose at rates many orders of magnitude greater than those of the dihydro analogs. (For example, the decomposition of 2,3-diazabicyclo [2.2.2] oct-2-ene is slow below 100°[10]). It is reasonable to conclude that some of the thermodynamic driving force is effective in lowering the transition state energy in the unsaturated cases because all three of the bonds ultimately to be broken (the C–C pi bond and the C–N sigma bonds) are partially broken in the transition state, that is, the reaction is a concerted Diels–Alder cycloreversion.[8,9]

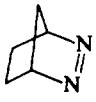
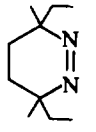
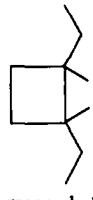
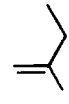
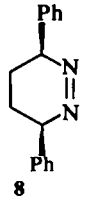
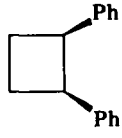
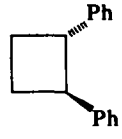
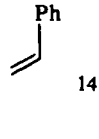
Unlike the saturated analogs, *e.g.*, **6**,[11,12] **7**,[13] and **8**,[14] all of which give ring-closure products (Table 1), the unsaturated azo compounds give none. If diradical intermediates such as **9** and **10** are the precursors of the ring-closure products,[11-14] the hypothetical diradical counterparts in the unsaturated series must have either a drastically lowered ratio of rate constants for ring-closure *vs* bond cleavage (for some not very obvious reason), or more probably, are simply by-passed in favor of a concerted mechanism.



9 10

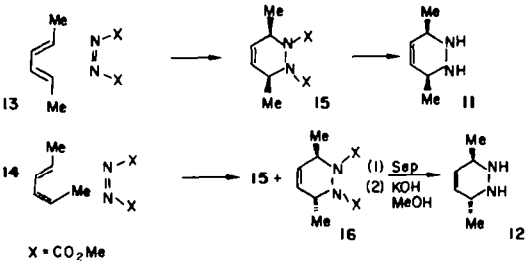
Finally, the weak stereospecificity of ring-closure in the saturated cases (Table 1) is consistent with a diradical intermediate such as **9**, which could suffer internal rotations. To complete the logical matrix of three criteria and two mechanisms, it is necessary only to determine the stereochemistry of the fragmentation reactions. This important problem has not yet been solved in the saturated series, where it could give insight, for example, on whether the ring-closure and fragmentation products arise from a common intermediate diradical. However, as the following section shows, the unsaturated series does conform to the highly stereospecific pattern expected from the concerted mechanism.

Table 1. Hydrocarbons produced from pyrolysis of Azo compounds

Reactant	Product, % of hydrocarbons closure	fragment.	Ref
 **6**	 100	 0	11, 12
 7 meso d, l	 meso d, l 43 2·5 3·5 42	 49 51	13
 **8**	 25	 14	 61 14

Thermal decomposition of stereochemically labeled 1,2-diazacyclohexa-1,4-dienes[15]

The syntheses of the hydrazo precursors of *cis*- and *trans*-3,6-dimethyl-1,2-diazacyclohexa-1,4-dienes (**11** and **12**) are accomplished by Diels–Alder addition of *trans, trans*- and *cis, trans*-hexa-2,4-diene (**13** and **14**), respectively, to dimethyl azodicarboxylate. The addition of the *trans, trans*-compound **13** is rapid and exothermic, and it gives only the *cis* diester **15**.[16] The *cis, trans*-compound **14** reacts more sluggishly. The reaction requires prolonged heating, and the product is a mixture of Diels–Alder adducts and "ene" adducts. Moreover, the Diels–Alder product, formed in 52% yield, is a mixture of the *trans*-adduct **16**, expected by analogy to the usual *cis*-on-the-diene stereochemistry,[17] and the *cis*-adduct **15** in a ratio of 4:1.

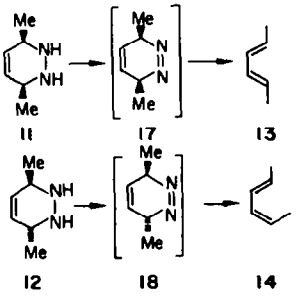


Among the interpretations (for the present, purely speculative) that might be advanced for this unusually low stereospecificity is the possibility that some of the reaction takes place by an orbital-symmetry allowed but experimentally unprecedented concerted *trans*-addition on the diene. Alternatively, and perhaps more reasonably, part or all of the addition to **14** may proceed by a radical chain mechanism, not unlike that which is involved in "ene" reactions of azodicarboxylic ester.[18]

The proportion of the desired *trans*-diester **16** in the **15**:**16** mixture can be improved to about 90% by irradiation of a mixture of **14** and dimethyl azodicarboxylate, but the overall yield of Diels–Alder type adducts falls to 34%.

Fortunately, the *trans*-diester **16** is a solid and can be purified readily by recrystallization. Saponification of the pure *cis*- and *trans*-diesters, **15** and **16**, gives the respective hydrazo compounds, **11** and **12**, as air-sensitive materials which can be stored under nitrogen at room temperature.

Oxidation of an ether solution of the *cis*-hydrazo compound **11** by yellow mercuric oxide or manganese dioxide gives a nearly quantitative yield of nitrogen, presumably *via* the very unstable azo compound **17**. Gas liquid chromatography (GLC) of the solution shows *trans, trans*-hexa-2,4-diene, **13**, as the only volatile organic product under analytical conditions that would reveal as little as 0·1% of *cis, trans*- or *cis, cis*-hexa-2,4-diene. Similarly, oxidation of *trans*-hydrazo compound **12** gives only *cis, trans*-hexa-2,4-diene, **14**.*

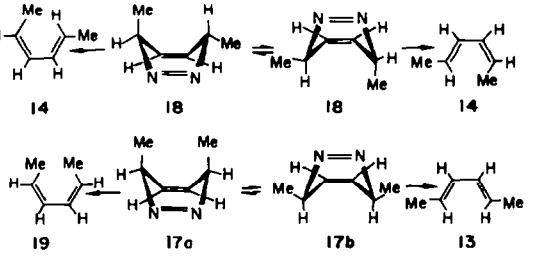


Attempts to detect the presence of the azo compounds, **17** and **18**, by carrying out the oxidations at low temperature are unsuccessful. Even at −50°, no indication can be found of the UV absorption that such substances should show. Presumably, the azo compounds do not survive for even the few seconds necessary to make the spectroscopic measurements.

The exceptional speed of these decompositions and the complete stereospecificity strongly suggest that the C=C double bond of **17** and **18** participates in both the rate- and product-determining steps of the reactions.

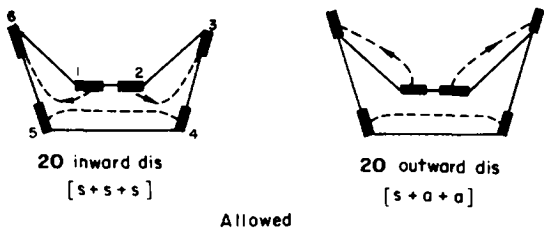
Two stereochemical points are important. First, the decompositions of **17** and **18** are retro-Diels–Alder reactions in which the leaving dienophile (N_2) departs by a pathway that is strictly *cis* on the diene in both cases. This is to be contrasted with the weak stereospecificity observed in the forward Diels–Alder reaction of one of the same dienes, **14**, with dimethyl azodicarboxylate.

Second, although the *cis*-on-the-diene stereochemistry can lead from the *trans*-azo compound **18** only to *cis, trans*-hexa-2,4-diene **14**, in principle it can lead to either *trans, trans*- or *cis, cis*-hexa-2,4-diene, **13** or **19**, from the *cis*-azo compound **17**. The exclusive formation of the *trans, trans* product **13** and the strict avoidance of the *cis, cis*-product **19** must be due to severe steric repulsions between the Me groups. These groups occupy



*The stereospecificity is reminiscent of that observed in the decompositions of diazenes[19] and sulfolenes,[20] although the latter two reactions are more properly named cheletropic[21] rather than retro-Diels–Alder.

unfavorable flagpole-type positions in the *cis, cis*-transition state, which must have a conformation similar to **17a**. On the other hand, the *trans, trans*-transition state must resemble conformation **17b**, in which the Me–Me repulsion is absent. As we shall see, stereoelectronic factors in other systems make it possible to override this steric effect.



Theoretical analysis of the [σ2 + σ2 + σ2] *cycloreversion of cyclohexane*

Before a description of the practical aspects of the replacement of the C–C pi bond of **17** and **18** by a sigma bond, it may be instructive to consider the hypothetical "explosion" of cyclohexane itself in some detail. Although Woodward and Hoffmann already have given an introduction to the orbital symmetry aspects of this subject,[22a] our discussion modifies theirs somewhat for the general case and also provides a basis for subsequent consideration of the special structural features of the molecules used in our experiments.

Imagine that cyclohexane is to decompose by a boat-shaped transition state, **20**. For convenience, we use the term[22a] "backbone bond" to refer to the unique one of the breaking bonds (C_1–C_2), and the term "side bonds" to refer to the other two (C_3–C_4 and C_5–C_6), which are geometrically identical to each other but different from the backbone bond. The Woodward–Hoffmann discussion[22a] sets up a distinction between two allowed processes in which the backbone bond breaks by disrotation. In one of these, the rotation is inward, toward the under side of the cyclohexane cup. In the other, the rotation is outward. The original treatment[22a] describes the two reactions as shown in **20**, inward [s + s + s] and outward [s + a + a], both reactions being orbital symmetry allowed. It also points out that the [s + s + s] rotation should be favored because it more rapidly develops overlap between the orbitals destined to form the product pi bonds (between C_1–C_6 and C_2–C_3).

However, we must note that the designations [s + s + s] and [s + a + a] are purely arbitrary in the present case. For example, it is perfectly permissible to switch the facialities so as to write an inward-disrotation using the combination [s + a + a] or an outward disrotation using [s + s + s] (see **21**).* It follows that no stereochemical experiment is capable of distinguishing the [s + s + s] from the [s + a + a] mode in the cyclohexane decomposition. The distinction between inward and outward rotations remains valid, however.†

Table 2. Stereochemical pathways in the [σ2 + σ2 + σ2] cycloreversion

Olefin stereochem[a]			Pathway	Symmetry nomenclature	Assignment
4, 5	2, 3	1, 6			
C	C	C	inward dis[b]	sss or saa	allowed
C	C	T	con[c]	ssa or aaa	forbidden
C	T	C	con[c]	ssa or aaa	forbidden
C	T	T	outward dis[d]	saa or sss	allowed
T	C	C	inward dis[b]	ssa or aaa	forbidden
T	C	T	con[c]	saa or sss	allowed
T	T	C	con[c]	saa or sss	allowed
T	T	T	outward dis[d]	ssa or aaa	forbidden

[a] Stereochemistry of the olefin product relative to that of the cyclohexane at the indicated carbons. "C" means retention, "T" means inversion.

[b] Inward disrotation at C_1 and C_2 or outward disrotation at C_3 and C_6.

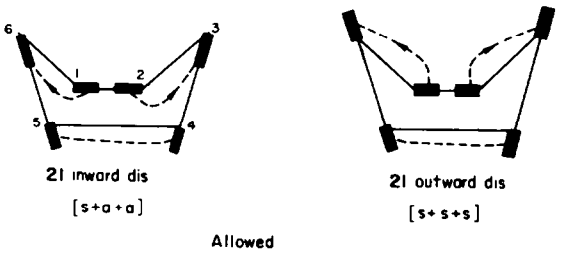
[c] Conrotation at C_1 and C_2 or at C_3 and C_6.

[d] Outward disrotation at C_1 and C_2, or inward disrotation at C_3 and C_6.

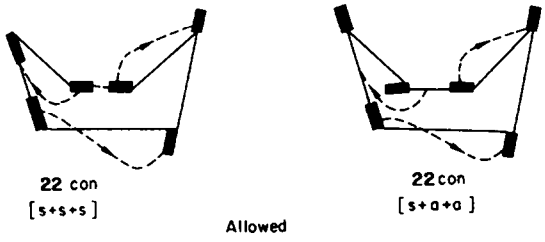
*Here, as elsewhere,[22b] diagrams showing the faces of reaction elements are constructs of convenience and do not represent molecular orbitals.

†It should be obvious that inward rotations of both C_1 and C_2 cannot be distinguished by stereochemical means from outward rotations of both C_3 and C_6, and *vice versa*.

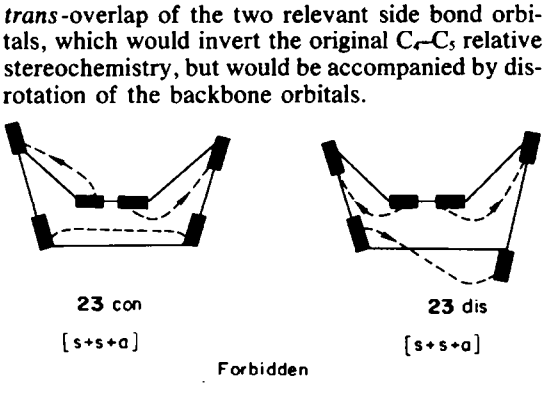
In addition to these two orbital symmetry allowed processes, both of which are disrotatory, there is, at least formally, another allowed path involving *trans* overlap of the two side bond orbitals



in one olefin fragment. This would invert the original C_4–C_5 relative stereochemistry and would be accompanied by a conrotation of the backbone orbitals (or of the C_3 and C_6 orbitals). Just as in the case of the disrotatory processes, the conrotatory allowed one can be represented as [s + s + s] or [s + a + a] (**22**-con).



There are two forbidden pathways, both of which can be described as either [s + s + a] or [a + a + a]. One of these (see **23**-con) involves *cis*-overlap of the two side bond orbitals destined to form the new pi bond between C_4 and C_5 in one olefin fragment. This would preserve the original C_4–C_5 relative stereochemistry but would be accompanied by a conrotation of the backbone orbitals (or of the C_3 and C_6 orbitals). The other (see **23**-dis) involves *trans*-overlap of the two relevant side bond orbitals, which would invert the original C_4–C_5 relative stereochemistry, but would be accompanied by disrotation of the backbone orbitals.



*The conformation shown for these bicyclic compounds is one of several that can exist in each case and is not necessarily the most stable one. Some information on conformational aspects of the homologous cyclobutyl series is given by a variable temperature NMR study.[23]

Table 2 lists the eight results possible in principle from the fragmentation of a fully labeled cyclohexane. We may divide these for convenience into two groups, one in which the olefin formed from C_4–C_5 retains the original relative configuration (C), and the other in which the configuration is inverted (T). The latter group may be considered to be generally unfavorable in the boat geometry, because the projected angle between the orbital lobes in the side bonds must contract from about 180° in the cyclohexane to 0° in the olefin.

Within each group, the allowed and forbidden sub-groups are distinguishable experimentally. In the 4,5 (C) group, inward and outward disrotation both are allowed, and conrotation (either of two kinds) is forbidden. In the 4,5 (T) group, the conrotations are allowed and the disrotations forbidden.

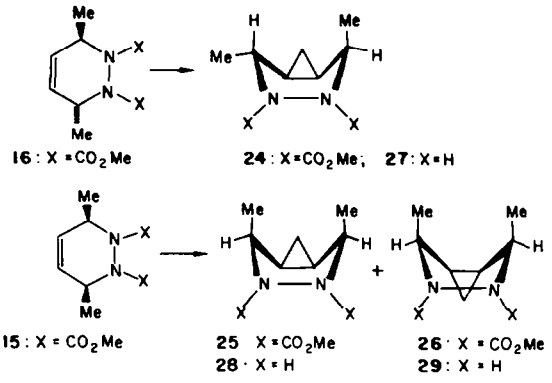
The nomenclatural ambiguity shown in Table 2 is quite general and is, of course, merely an artifact of this particular form of the Woodward–Hoffmann Rules. The following *theorem*, in support of which we offer only the absence of disproof by counterexample, seems intuitively correct. It may be helpful as a codicil when the rules are to be applied using the 2_s and 2_a convention.

A description may be defined as a listing of the suprafacial and antarafacial 2-electron reaction components, regardless of the sites of particular faciality, e.g., $[2_s + 2_s + 2_s + 2_s]$. *Every allowed thermal reaction may be described as a process involving* m *2-electron components, of which an odd number must be suprafacial. The stereochemistry of an allowed reaction corresponds to any of* (m + 1)/2 *experimentally indistinguishable descriptions if* m *is odd, and to any of* m/2 *such descriptions if* m *is even. As a corollary, it follows that for a given value of* m, *all allowed stereochemical pathways have the same set of descriptions.*

Replacement of C–C pi *bond of the* 1,2-*diazacyclohexa*-1,4-*dienes by a sigma bond. The homo-Diels–Alder cycloreversion of diazabicyclo* [4.1.0] *heptenes*[15,24]

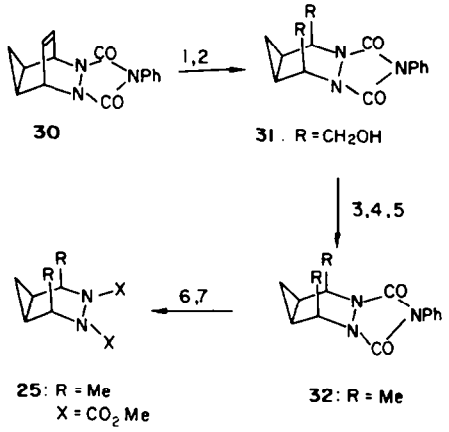
The cupric chloride-catalyzed action of diazomethane on the *trans* diester **16** gives the diazabicyclo [4.1.0] heptene diester **24** as the sole cyclopropanation product. From the same treatment of the *cis*-diester **15** there is obtained a mixture of two isomers, one of which must be the *syn*, *cis*-**25** and the other the *anti*, *cis*-**26** diester, in the ratio of about 1:8.* Separation of **25** and **26** by GLC gives the pure materials.

The NMR spectra of the two *cis* compounds **25** and **26** do not lead to an unambiguous assignment of stereochemistry. It is reasonable to suppose that the major cyclopropanation product from **15** should be the *anti*, *cis*-isomer **26**, since it would be formed by attack on the sterically less hindered side of the double bond. This assignment can be confirmed by an independent synthesis (Scheme 1) of the minor



isomer **25** from the cycloheptatriene -N-phenyltriazolinedione adduct **30**.[15]

The *syn* relationship of the cyclopropane ring and the unsaturated bridge in **30** previously proposed[25] is confirmed by the differences in the NMR spectra of **30** and its dihydro derivative, obtained by diimide reduction of the double bond. The chemical shifts of the cyclopropane methylene hydrogens in the dihydro compound lie at much lower fields (0·5 ppm for the *endo* proton and 0·2 ppm for the *exo*) than those of **30**, suggesting that in **30** these protons lie close to the pi electrons of the double bond and hence are strongly shielded.

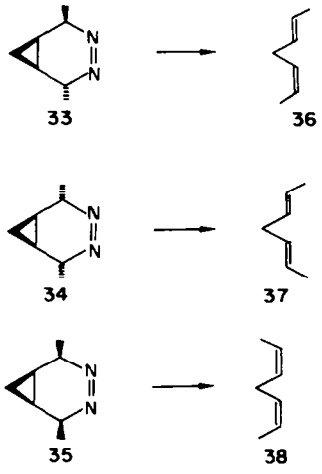


SCHEME 1

1, O_3; 2, $NaBH_4$; 3, MesCl; 4, EtSNa; 5, Raney nickel; 6, KOH; 7, $ClCO_2Me$

The two carbons of the *syn*-unsaturated bridge of **30** can be turned into a pair of *syn*-Me groups by a sequence beginning with cleavage of the bridge by ozonolysis and $NaBH_4$ reduction to give the crystalline diol **31**. Successive steps as shown in Scheme 1 give the dimethyl triazolinedione **32**, which in two more steps is converted to the diester **25**, identical in all respects with the minor cyclopropanation product from **15**.

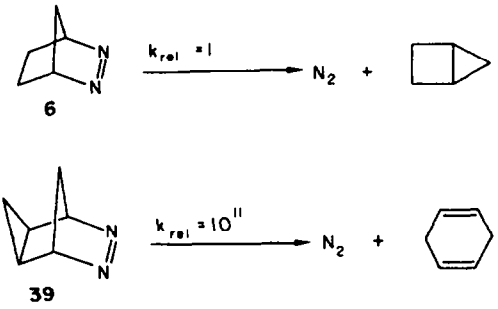
Procedures analogous to those used in the olefinic series convert the three bicyclic diesters **24**, **25**, and **26**, to hydrazo compounds, which are oxidized as before. The azo compounds, **33**, **34**, and **35**, can be observed by both UV and NMR spectroscopy at temperatures below −70°, but they decompose gradually at −10° ($t_{1/2} \sim 30$ min) and rapidly at room temperature to nitrogen and hepta-2,5-dienes. The formation of these dienes is again highly stereospecific, the *trans, anti-cis*, and *syn-cis*-azo compounds **33**, **34**, and **35**, giving respectively *cis, trans*-, *trans, trans*-, and *cis, cis*-hepta-2,5-diene (**36**, **37**, and **38**), each in >99·5% isomeric purity.



The results meet all three criteria for a concerted homo-Diels–Alder cycloreversion, enhanced rate of decomposition, absence of ring-closure products, and high stereospecificity. Although data permitting comparisons at a common temperature are not available, it is clear that the model unactivated diazacyclohexenes (*e.g.*, the 3,6-dimethyl-3,6-diethyl compounds, **7**, Table 1) which decompose at convenient rates at 140° must be many orders of magnitude less reactive than the bicyclic cyclopropane series **33–35**. The hypothetical ring-closure products from **33–35**, the 2,3-dimethylbicyclo [2.1.0] pentanes, prepared by independent synthesis,[26] are all stable under the conditions of these decompositions, but are not found there.

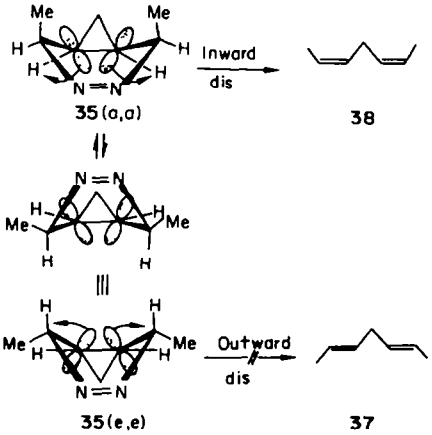
The important studies of Allred *et al.*[31] have demonstrated cyclopropane bond participation in some azo compound decompositions by the absence of ring-closure products and by enormous rate enhancements, exemplified by the comparison of compounds **6**[11,12] and **39**[31a]. Although the stereochemical criterion cannot be applied here, the results for **39** and its relatives seem best interpreted as concerted decompositions.

As Table 2 shows, it would be necessary to know the stereochemistry at each of the carbons of a



cyclohexane to assign the process as orbital symmetry allowed or forbidden. With our system, of course, this is not possible, because the role of the C_4–C_5 bond in the hypothetical fully labeled cyclohexane of Table 2 is played by the N=N bond of our azo compounds. This precludes any direct deduction of the stereochemistry at that site. However, it is reasonable to assume that the decomposition involves *cis* nitrogen orbitals, not only because a 180° rotation would be required for *trans* orbitals (the reason already mentioned in the cyclohexane case), but also because such a rotation would require disruption of the azo N=N pi bond.[24]

Independent of this assumption, the stereospecificities in the cycloreversions of **33**, **34**, and **35** show a strong preference for the inward-disrotatory mode over either the outward-disrotatory or the conrotatory mode. In each case, the preferred transition state seems to be one in which nitrogen departs *anti* to the cyclopropane ring.* The decomposition of the *syn-cis*-azo compound **35** forcefully illustrates this preference. The inward-disrotatory transition state in this case, which leads exclusively to *cis, cis*-hepta-2,5-diene **38**, places two Me groups in a near *axial–axial* conformation, where there must be severe steric repulsions. These are similar to repulsions that strictly



*For similar behavior in cheletropic reactions, see Refs 27 and 28.

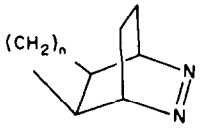
preclude the formation of any *cis, cis*-hexa-2,4-diene in the decomposition of the monocyclic azo compound **17**, which gives the *trans, trans*-diene instead. The stereoelectronic benefit of effective orbital overlap in the inward-disrotatory transition state derived from bicyclic azo compound **35(a,a)** is enough to override the unfavorable steric effect.

The orbital overlap effect favoring inward disrotation in the hypothetical decomposition of the parent cyclohexane noted by Woodward and Hoffmann is reinforced in these bicyclic compounds, because the backbone bond (the bridge bond) is bent,[29] being part of a cyclopropane. Thus, the axes of the p orbitals used to construct the Walsh model of the cyclopropane[30] in **35(aa)** are nearly parallel to those of the breaking C–N bonds, whereas in **35(e,e)** the conformer leading to outward disrotation, the projected axes are nearly perpendicular.

How important is this bent character of the backbone bond in facilitating concert? As a first step in an approach to this question, we examine the effect of replacement of the cyclopropane unit of **33**, **34**, and **35** by a cyclobutane ring, as in a diazabicyclo [4.2.0] octene.

Replacement of the cyclopropane ring of the diazabicyclo [4.1.0] *heptenes by a cyclobutane ring. The cycloreversions of diazabicyclo* [4.2.0] *octenes*[32]

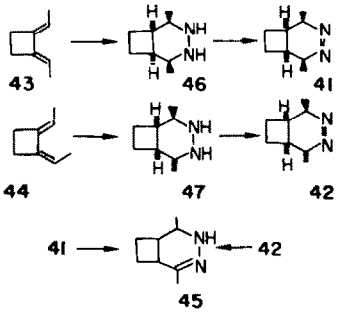
This replacement should decrease the bent character[29] of the bridge bond, weaken its overlap with the two breaking C–N bond orbitals in the transition state, and thereby narrow not only the energy gap between the concerted and nonconcerted paths but also that between the concerted and nonconcerted ones. Some indication that the borderline with a nonconcerted process may have been reached in a cyclobutane analog is suggested by the behavior of compound **40b**, which decomposes much more slowly than does its cyclopropane analog **40a** and is reported to form ring-closure products.[31d,e]



40 a: n = 1
b: n = 2

Two compounds appropriate for the application of the three criteria to a test of the bent bond requirement are *syn, cis*- and *trans*-2,5-dimethyl-3,4-diazabicyclo [4.2.0] oct-3-ene, **41** and **42**. The syntheses of these compounds by highly stereospecific methods from the readily available[33] isomeric dienes **43** and **44** are described elsewhere.[23,32] We must emphasize, however, that manipulations in

the cyclobutane series encounter all of the difficulties traditionally associated with azo compounds containing enolizable hydrogens.[10,12,14] Whereas the nitrogen-releasing decompositions in the unsaturated (**17**, **18**) and cyclopropane (**33**, **34**, **35**) series are so fast that prototropic shift to a hydrazone cannot be observed, the rate of loss of nitrogen is much slower in **41** and **42**. As a consequence, irreversible tautomerization to the crystalline hydrazone **45** becomes a serious problem. Traces of acid or base, heating or storage in neutral solvent, or irradiation all convert the azo compounds **41** and **42** to the hydrazone.

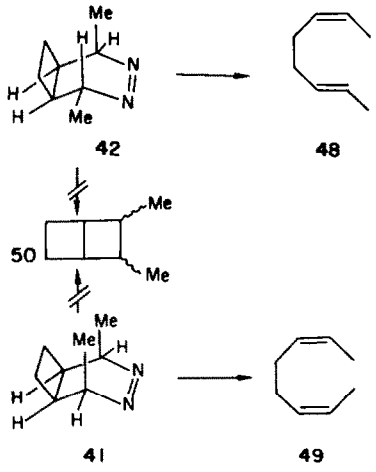


Successful syntheses and reactions of azo compounds **41** and **42** can be achieved by vacuum line techniques.[23,32] Preparation and sublimation under rigorously anaerobic conditions give beautifully crystalline pure samples of the corresponding hydrazo compounds **46** and **47**. Either of these materials, when treated in pure benzene-d_6 with oxygen, is converted to a solution of the corresponding azo compound in good yield. The azo compounds are stable enough to permit NMR and UV spectroscopic confirmation of their presence.

For pyrolysis, these solutions are injected into an evacuated Pyrex chamber pre-heated to 200°. The initial pyrolysis pressures are 100–400 nm, and the rates of decomposition are not sensitive to surface or to pressure in this range. Collection of the products in a trap at −196° gives a mixture of hydrazone **45** and octa-2,6-diene. In the most favorable runs, the yield of diene is about 40%.

The reactions are completely stereospecific. The *trans*-azo compound **42** gives exclusively *cis*, *trans*-octa-2,6-diene **48**, and the *syn-cis*-azo compound **41** gives exclusively *cis*, *cis*-octa-2,6-diene **49**. Cross contamination of the two diene products with each other or with *trans*, *trans*-octa-2,6-diene amounts to 0·1% at most. None of the ring-closure products, the 2,3-dimethylbicyclo [2.2.0] hexanes **50** is formed. Control experiments show that pyrolysis of the isomers of structure **50** is slow under these conditions and that neither any of these isomers nor the hydrazone **45** is an intermediate in the formation of the dienes **48** and **49**.

The stereochemistry of these decompositions is exactly analogous to that observed in the cyclo-

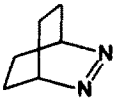


propane series, **33**–**35**. Despite the decreased bent bond character in the backbone bond of the cyclobutane analogs, there is no *discernible* decrease in stereospecificity. Since both series have stereospecificities that are "off-scale" with regard to the available experimental techniques, however, any real differences that may exist cannot be detected. As before, the inward-disrotatory path predominates heavily, even in the face of the strong steric repulsions that must be overcome in the transition state from the *cis*-compound **41**.

Despite the high stereospecificity in the cyclobutane series, there is a marked rate depression ($t_{1/2}$ for **41** ~ 1 min at 200°) as compared to the analogous cyclopropanes ($t_{1/2}$ for **33** ~ 30 min at − 10°) and olefins ($t_{1/2}$ for **17** < 1 min at − 50°). Since activation energies are not available for these compounds, rate comparisons at a common temperature are not possible, but the effects are large and unmistakable.

Our diazabicyclo [4.2.0] octene **41** decomposes at about five times the rate of Allred's cyclobutane derivative **40b**. Both are somewhat more reactive than the unsubstituted model compound **51** and very much less reactive than Allred's cyclopropane **40a**.

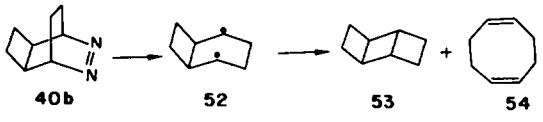
Allred and Hinshaw[31d,e] report a large difference in activation entropy between the decompositions of **40a** ($\Delta S^{\neq} = -21$ e.u.) and **40b** ($\Delta S^{\neq} = +10{\cdot}5$ e.u.) and note that the latter value is very close to that of the model compound **51** ($\Delta S^{\neq} = +11$ e.u.). They propose that this difference arises from a difference in mechanism, the decompositions of **40b** and **51** being stepwise reactions *via* hydrocarbon diradical



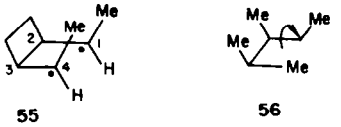
51

intermediates (*e.g.*, **40b** → **52**). They also report that pyrolysis of **40b** gives the tricyclic ring-closure product **53** that would be expected from the diradical **52**, in addition to the diene product **54**.

In our own case, it is more difficult to support a diradical interpretation. This would require that the hypothetical intermediate from **41** be formed in conformation **55** and that cleavage of the backbone bond (C_2–C_3) in **55** be at least 1000 times as fast as stereorandomizing bond rotations. There are good reasons to believe[34] that there would be no significant rotational barriers introduced by conjugation



40b **52** **53** **54**



55 **56**

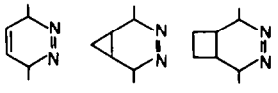
of the odd electron centers at C_1 and C_4 with the cyclobutane ring orbitals of **55**. In the absence of such special effects, internal barriers about C_α–C_β bonds in hydrocarbon radicals may be estimated to be no more than about one-sixth of those in the corresponding hydrocarbons.* The barrier for the rotation shown in the model hydrocarbon 2,3-dimethylpentane **56** is 7 kcal/mole,[37] from which we may estimate that the barrier to rotation about the C_1–C_2 bond of the hypothetical diradical **55** would be $\leqslant$ 1·2 kcal/mole. The 1000-fold stereospecificity of diene formation corresponds (at 200°) to $\Delta\Delta F^{\ddagger} \geqslant$ 6·5 kcal/mol. That is, $\Delta F^{\ddagger}$ for cleavage of the C_2–C_3 bond would have to be 6·5 kcal/mol *lower* than $\Delta F^{\ddagger}$ for bond rotation, which would require that $\Delta F^{\ddagger}$ for cleavage have a *negative* value, if the estimate of $\leqslant$ 1·2 kcal/mole for the rotational barrier is even approximately correct. It is conceivable that "through-bond" coupling might increase the rotational barrier,[38] but the peculiar requirements that the diradical be formed exclusively in conformation **55** and that it fail to cyclize to 2,3-dimethylbicyclo [2.2.0] hexanes **50** would remain.† We therefore interpret the decompositions of **41** and **42** as concerted reactions.

CONCLUSION AND PROSPECT

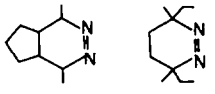
The thermal decompositions of cyclic azo compounds can be facilitated by participation of a pi or bent sigma backbone bond. The rate falls off steeply from pi to cyclopropane to cyclobutane (**57** > **58** > **59**), although the stereospecificity remains high throughout. These reactions all appear to be concerted [2 + 2 + 2] cycloreversions, with the degree of concert gradually diminishing as the backbone bond orbital acquires more sigma character. The cyclobutane series **59** must be borderline cases, since Allred's closely analogous substance **40b** seems to employ a nonconcerted mechanism of decomposition, at least in part.

Would some degree of concert be left if the backbone bond were pure sigma, that is, if the orbital axis were coincident with the bond direction? If so, there would be a chance to test the primitive form of Woodward and Hoffmann's intriguing prediction that the $[\sigma 2 + \sigma 2 + \sigma 2]$ cycloreversion should favor the inward disrotation.

There seems but a slim hope that concert may survive in the pure sigma system. The decomposition of the Bartlett–Porter saturated azo compound **7**, for example, already has been consigned across the mechanistic borderline into diradical territory.[13] As we have mentioned, however, it would be of great interest to have information on the stereochemical course of a pure (or nearly pure)



57 **58** **59**



60 **7**

sigma cycloreversion. For this purpose, it probably would be best to change the system to one which is similar to that in **57**, **58**, and **59**, in order to avoid the complications associated with varying degrees of substitution at the potential radical centers.[39] The obvious candidate is the cyclopentano compound **60**. The study of this deceptively simple substance would be a formidable objective, since there is every reason to believe that its cycloreversion would be slow and its irreversible tautomerization to a hydrazone would be fast. Unless a more practical way of arming the cyclohexane "explosion" could be found, for example, by using a leaving group other than molecular nitrogen, a would-be-solver of this problem might not be able to avoid these obstacles easily.

*The following values (in kcal/mol) are illustrative: propane (2·8), propyl radical (0·4–0·5); isobutane (3·6); isobutyl radical (0·3).[35,36]

†Roth and Martin[40] find substantial quantities of *cis-endo*- and *cis-exo*- **50** in the pyrolysis products from 5,6-dimethyl-2,3-diazabicyclo [2.2.2] oct-2-ene, a reaction which they interpret as passing over a 2,3-dimethylcyclohexane-1,4-diyl diradical. This suggests that there are no insuperable steric barriers opposing the formation of **50**, which therefore is a reasonable product to expect from diradical **55**.

Acknowledgments—This work was supported in part by grants from the National Institute of General Medical Sciences (GM-16962), the National Science Foundation (GP-11017X and GP-33909X), the Petroleum Research Fund, administered by the Americal Chemical Society, and the AFOSR (SRC), U.S. Air Force Grant No. 68-1358. We are grateful to these agencies for their support.

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