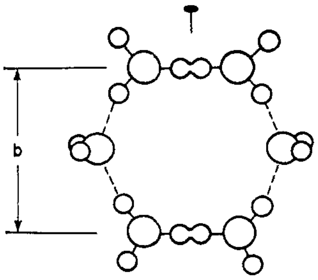

Figure 2. $[H_5O_2]^+$ groups assembled into a ring which is a link of a chain extending along *b*. The repeating unit is $[H_9O_4]^+$. The H_2O molecules which bind the $[H_5O_2]^+$ groups together are rather loosely held and display large thermal motion. Large circles are oxygen and small circles hydrogen atoms.

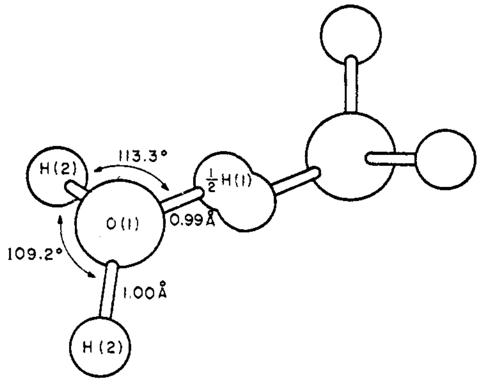

Figure 3. Configuration of the $[H_5O_2]^+$ ion. The two O(1) and the two ½H(1) sites are coplanar. The four H(2) sites are symmetry related. The group configuration is strictly *trans*. The O–O separation is 2.57 ± 0.01 Å and the O–H···O angle is 172°.

which is a link in the protonated water molecule chain. Hydrogen-bonding interactions between adjacent chains as well as those between adjacent $(AuCl_4)^-$ and $[(H_5O_2)^+ \cdot 2H_2O]$ layers appear to be weak or absent.

The most interesting structural feature is the $(H_5O_2)^+$ group which is illustrated in Figure 3. The required symmetry of the group is 2/m and the configuration is *trans* as indicated. The bridging proton, originally expected to be centered, definitely refined to disordered, off-bond-line positions with a site separation of 0.62 Å.

This rather remarkable configuration raises interpretative problems. There is an intriguing similarity between the now well-known pyramidal oxonium ion and the two symmetry related halves of the $(H_5O_2)^+$ group described here. This suggests that $(H_5O_2)^+$ is simply $(H_3O^+ \cdot H_2O)$. The static disorder which this implies and the nonequivalence of the three O–H···O bonds involved tend to weaken this interpretation. We prefer to consider the grouping a variant of the diaquated proton[8] with an unusual symmetrical double-well potential. The dynamic disorder implied in this interpretation should be verifiable by spectroscopic measurements. Such measurements are now in progress.

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[8] J. M. Williams, "Proceedings of the Second Materials Research Symposium, 1967," Special Publication No. 301, National Bureau of Standards, Washington, D. C., in press.

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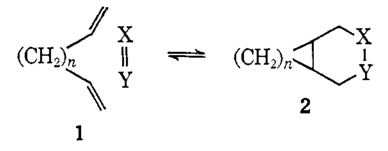
The Geometry of the Transition State of the Retrograde Homo Diels–Alder Reaction. A Stereospecific Conversion of 1,3- to 1,4-Dienes[1]

Sir:

The efficiency with which a small ring transmits conjugative and orbital symmetry influences can be evaluated from a knowledge of the stereochemistry of the homo Diels–Alder reaction (**1** ⇌ **2**). The present work describes a solution of this problem for the retrograde (**2** → **1**) monohomo case (n = 1).[2] The results demonstrate that a cyclopropane ring exerts strict control of the stereochemistry of the olefinic product, even in the face of strongly countervailing steric effects. They also provide a stereospecific synthetic method for homologation of 1,3-dienes to 1,4-dienes.



Model studies of ordinary Diels–Alder retrogression show a high degree of stereospecificity. Thus, oxidation of the *cis* hydrazo compound **3** by air, or preferably of an ether solution by yellow mercuric oxide or manganese dioxide in the presence of anhydrous sodium sulfate at 25°, gives a nearly quantitative yield of nitrogen, presumably *via* the very unstable azo compound **4**. Vapor chromatography (vpc) of the solution shows *trans,trans*-2,4-hexadiene (**5**) as the only volatile organic product under analytical conditions that would reveal 0.1% *cis,trans*- or *cis,cis*-2,4-hexadiene. Similarly, oxidation of *trans*-hydrazo compound **6** gives only *cis,trans*-2,4-hexadiene (**8**).[3–8] The ultraviolet chromophore of the presumed azo compounds **4** and **7** is not observed, even at −50°. The exceptionally high rate[9] and stereospecificity suggest double bond participation in both the rate- and product-determining steps of the decomposition of **4** and **7**. Although one cannot strictly exclude a two-step mechanism with an intermediate (*e.g.*, **11**) in which loss of nitrogen is much faster than bond rotation, a simple and conceptually economical alternative would picture the reaction as a concerted, orbital-symmetry-allowed[10] retro-Diels–Alder process.

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[1] This work was supported in part by grants from the Petroleum Research Fund and the AFOSR (SRC)-OAR, U. S. Air Force Grant No. 68-1358.

[2] During our study, W. L. Mock, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P-20, reported some stereochemical results of the analogous decomposition of 3-bicyclo[3.1.0]thiahexane 3,3-dioxides.

[3] Hydrazo compounds **3** and **6** result from hydrolytic decarboxylation of the corresponding esters, **9**[6] and **10**.[5] Compound **9** is formed in virtually quantitative yield from the reaction of **5** and dimethyl azodicarboxylate;[6] **8** and dimethyl azodicarboxylate react more sluggishly to give a 4:1 mixture of **10** and **9** (boiling benzene, 18 hr).

[4] Diazenes[7] and sulfolenes[8] behave analogously.

[5] Elemental analysis confirms the composition.

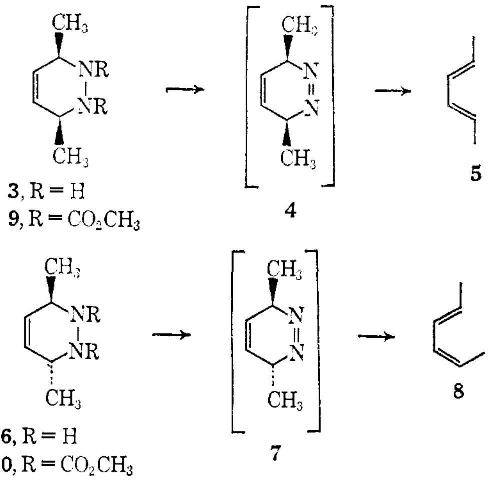
[6] R. Daniels and K. A. Roseman, *Tetrahedron Letters*, 1335 (1966).

[7] D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

[8] (a) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966); (b) W. L. Mock, *ibid.*, **88**, 2857 (1966).

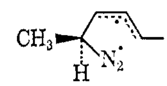
[9] Saturated analogs do not decompose at appreciable rates below 140° (see, *inter alia*, P. D. Bartlett and N. A. Porter, *ibid.*, 90, 5317 (1968)].

[10] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 15 (1968).



3, R = H
9, R = CO_2CH_3
4
5
6, R = H
10, R = CO_2CH_3
7
8

The CuCl-catalyzed action of diazomethane on the *trans* diester **10** in ether–pentane gives the *trans*-cyclopropane **12**;[5] on the *cis* diester **9**, it gives a mixture of one part of *syn-cis*-cyclopropane **13**[5] and eight parts of *anti-cis* **14**.[5] Separation of **13** and **14** is achieved by vpc on a Carbowax column.



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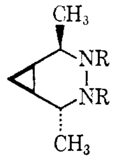
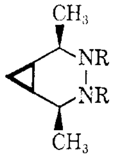
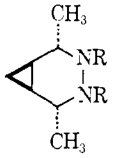


12, R = CO_2CH_3
17, R = H

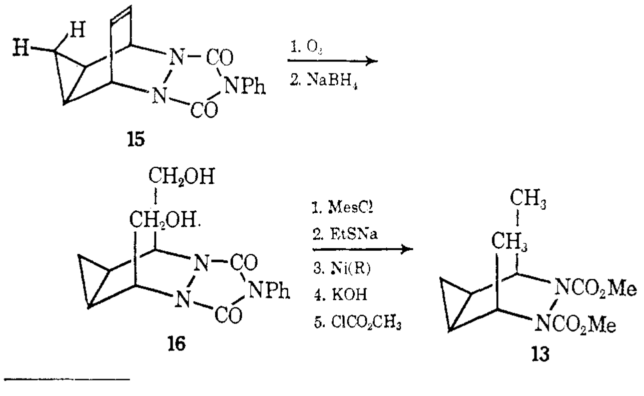


13, R = CO_2CH_3
18, R = H



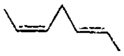
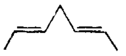
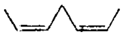
14, R = CO_2CH_3
19, R = H

The nmr spectra of the cyclopropanation products in the *cis* series **13** and **14** do not lead to an unambiguous assignment of stereochemistry, but the minor product is shown to be **13** by independent synthesis from the cycloheptatriene–N-phenyltriazolinedione adduct **15**.[11] The assignment[11] to **15** of the indicated orientation of the cyclopropane ring is confirmed by the observation that the nmr chemical shifts of the cyclopropane methylene hydrogens in **15** lie at much higher fields (0.5 ppm for *endo* and 0.2 ppm for *exo*) than those in the dihydro derivative obtained by diimide reduction of the double bond. Successive treatment of **15** with ozone and $NaBH_4$ gives the crystalline diol[5] **16**, from which **13** is derived by the steps shown.



Procedures analogous to those used in the olefinic series convert the three bicyclic diesters **12**, **13**, and **14** to the corresponding hydrazo compounds **17**, **18**, and **19**, which are oxidized as before. The azo compounds presumed to result are unstable at 25° and decompose smoothly to nitrogen and 2,5-heptadiene. Olefin formation is again highly stereospecific (Table I).

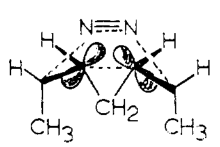
Table I. Products of Oxidation of Hydrazo Compounds

	 *cis, trans*[a]	 *trans, trans*[a]	 *cis, cis*[a]
17 (*trans*)	100	0[b]	0[b]
18 (*syn-cis*)	0[b]	1	99
19 (*anti-cis*)	0[b]	98	2

[a] Dienes independently synthesized by reductions of 2,5-heptadiyne with stereospecific alkylaluminum hydride reagents [*cf.* G. Zweifel and R. B. Steele, *J. Am. Chem. Soc.*, **89**, 5085 (1967)]. The nmr spectrum of the *trans,trans* diene is accurately simulated by a spectrum computed with the LAOCOON II program [A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964)], using reasonable coupling constants. [b] As little as 0.5% would be detectable.

The small amounts of cross products observed from **18** and **19** probably arise from small amounts of mutual cross-contamination of the two precursors **13** and **14**, which are difficultly separable by vpc.

The results are consistent with a concerted retrograde homo Diels–Alder mechanism. A strong preference is manifest for a transition-state geometry in which the nitrogen molecule departs *anti* to the methylene group of the cyclopropane ring. Especially noteworthy is the exclusive formation of *cis,cis*-2,5-heptadiene from *syn-cis*-hydrazo compound **18**, a reaction which passes over transition state **20** rather than its conformational isomer **21**. That **20** must involve a severe methyl–methyl repulsion is evident from the complete absence of *cis,cis*-2,4-hexadiene in the analogous oxidation of olefinic *cis*-hydrazo compound **3**. Clearly, some overriding influence is present in the bicyclic transition state. Although compensatory steric effects may make small contributions, the major factor is probably electronic. Apparently, in the bicyclic case, the requirement for orbital overlap of the three breaking bonds[12] is so stringent as to overcome the strain completely.



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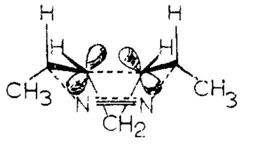

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(11) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 615 (1962).

(12) The large enhancement in the rate of thermal decarbonylation of *endo*-tricyclo[3.2.1.$0^{2,4}$]octen-8-one over its *exo* isomer is interpreted similarly [B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Am. Chem. Soc.*, **89**, 5964 (1967)].

(13) This investigation was supported in part by National Institutes of Health Postdoctoral Fellowship No. 2 FO2CA25233-02 from the National Cancer Institute.

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