Review

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Woodward and Hoffmann. Hoffmann and Woodward. A Close Collaboration Had Yet to Begin**

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Dedicated to the memory of Lionel Salem (1937 – 2024), a noted theoretical chemist, author, and scholar.

The History of the Woodward-Hoffmann Rules

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Abstract: In 1965, R. B. Woodward and Roald Hoffmann published five communications in the *Journal of the American Chemical Society* in which they outlined the mechanisms of electrocyclizations, cycloadditions, and sigmatropic reactions – today known as the Woodward-Hoffmann rules. Over the next several years, the organic chemistry community rushed to test the validity of the W–H rules and expand the range of reactions covered by them. Meanwhile, Woodward and Hoffmann were besieged with invitations to lecture and write expositions on these concepts. In this publication, I present an analysis of Woodward and Hoffmann's next publications in 1966 and 1967 on the W–H rules. Two of these publications were based on lectures Woodward or Hoffmann presented in late 1965 and 1966. I also discuss their own continuing research on the topic in this time period (all by Hoffmann; none by Woodward). I conclude that the assumed intimate collaboration of Woodward and Hoffmann had actually not yet begun.

Keywords: History of chemistry, Woodward-Hoffmann rules, pericyclic reactions, collaborations

"By the end of 1965, we had the main results, but it cannot be said that the overall picture, and how the different reactions "hung together," was clear. As we analyzed the different kinds of reactions, of course we used whatever quantum mechanical tools were at hand – frontier orbitals, correlation diagrams, orbital interactions analyzed with perturbation theory. But I don't think I had the story under complete control."[1,2] – Roald Hoffmann

1. Introduction

Between January 20, 1965, and October 5, 1965, Woodward and Hoffmann published five communications in the *Journal of the American Chemical Society* that explained the mechanism of electrocyclizations,[3] cycloadditions,[4] sigmatropic rearrangements,[5] the Alder *exo-endo* rule for the Diels-Alder reaction,[6] and the mechanism of the Cope reaction.[7] These publications were revolutionary. For the first time, they provided quantum chemical mechanisms for complex chemical reactions that were otherwise inexplicable by the heuristic (soft) explanations and reasoning by analogy that chemists had used for decades.[8] Indeed, the Woodward-Hoffmann (W–H) rules precipitated the quantum chemistry revolution in 20th Century science.[9] As Marshall Gates, then editor in chief of the *Journal of the American Chemical Society* (*JACS*) wrote to Woodward on the acceptance of the last two W–H communications,

"In my opinion, this is a remarkable series of Communications which have already forced a substantial revision in the thinking of serious organic chemists. You and Hoffmann are to be congratulated."[10]

As we well know, the Woodward-Hoffmann story did not end with their five 1965 *JACS* communications. Rather, the orbital symmetry story was just picking up steam. Table 1 lists all 14 of the Woodward-Hoffmann articles, including two manuscripts that were never published. Surely Woodward and Hoffmann's 1968 essay in the inaugural issue of *Accounts of Chemical Research*,[11] (W–H 10) and their 1969 treatise in *Angewandte Chemie*,[12] subsequently reprinted as a monograph in 1970,[13] are highlights of the Woodward-Hoffmann story.

Chronologically sandwiched between their five 1965 *JACS* communications (W–H 1 – W–H 5) and their *Accounts* and *Angewandte Chemie* masterpieces (W–H 10 and W–H 11) are four research documents, three authored by Hoffmann (W–H 6NP – W–H 8) and one by Woodward (W–H 9) between late 1965 and 1967. The research that led to these two publications and two unpublished manuscripts played important idiosyncratic functions in Woodward's and especially Hoffmann's personal and professional trajectories. The most subtle and unexpected back-story observation emanating from these four chronicles relates to the nature of the Woodward-Hoffmann collaboration (or lack thereof). The character of the W–H collaboration has previously been explored but only

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Table 1. Tabulation of the Woodward-Hoffmann publications, including lectures given by Woodward and Hoffmann on the topic that were published in their entirety. Items in pink are discussed in this publication.

	Date Received (and/or Accepted or Published) or Date Completed	Publication
The "Core" Publications		
W–H 1	Received Nov. 30, 1964 Published January 20, 1965	R. B. Woodward, R. Hoffmann, "Stereochemistry of Electrocyclic Reactions," *J. Am. Chem. Soc.* **1965**, *87*, 395–397.
W–H 2	Received March 22. 1965 Published May 5, 1965	R. Hoffmann, R. B. Woodward, "Selection Rules for Concerted Reactions." *J. Am. Chem. Soc.* **1965**, *88*, 2046–2048.
W–H 3	Received April 30, 1965 Published June 5, 1965	R. B. Woodward, R. Hoffmann, "Selection Rules for Sigmatropic Reactions, "*J. Am. Chem. Soc.* **1965**, *87*, 2511–2513.
W–H 4	Received August 16, 1965 Published Oct. 5, 1965	R. Hoffmann, R. B. Woodward, "Orbital Symmetries and *endo-exo* Relationships in Concerted Cycloaddition Reactions," *J. Am. Chem. Soc.* **1965**, *87*, 4388–4389.
W–H 5	Received August 16, 1965 Published Oct. 5, 1965	R. Hoffmann, R. B. Woodward, "Orbital Symmetries and Orientational Effects in a Sigmatropic Reaction," *J. Am. Chem. Soc.* **1965**, *87*, 4389–4390.
The "Treading-Water" Publications		
W–H 6NP	Summer to Autumn 1965. Not submitted. Sections inserted in other W–H publications.	R. Hoffmann, "Some Further Selection Rules for Concerted Cycloadditions"
W–H 7	Published in February 1966	R. Hoffmann, "The Electronic Structure of Some Transition States and Intermediates in Organic Reactions," *Trans. N.Y. Acad. Sci.* **1966**, *28 (Series II)*, 475–479.
W–H 8NP	Late 1965 to early 1966. Never submitted but inserted into drafts of the 1969 *Angewandte Chemie* treatise,[12] then deleted.	R. Hoffmann, "A Catalogue of Concerted Reactions"
W–H 9	Based on Woodward's lecture presented on July 8, 1966 Published 1967	R. B. Woodward, "The Conservation of Orbital Symmetry" in *Aromaticity, Publication No. 21*, The Chemical Society, London, **1967**, pp. 217–249.
The "Heart and Soul" Publications		
W–H 10	Received July 3, 1967 Published January 1, 1968.	R. Hoffmann, R. B. Woodward, "The Conservation of Orbital Symmetry," *Acc. Chem. Res.* **1968**, *1*, 17–22.
W–H 11a	Received January 7, 1969 Published November 1969	R. B. Woodward, R. Hoffmann, "The Conservation of Orbital Symmetry," *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781–853; *and* R. B. Woodward, R. Hoffmann, "Die Erhaltung der Orbitalsymmetrie," *Angew. Chem.* **1969**, *21*, 797–870.
W–H 11b	W–H 11a, reformatted and reprinted in monograph form, hardback and soft cover editions, 1970.	R. B. Woodward, R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie and Academic Press, **1970**.
W–H 12	Published February 6, 1970	R. Hoffmann, R. B. Woodward, "Orbital Symmetry Control of Chemical Reactions," *Science* **1970**, *167*, 825–831.
W–H 13a	Published in 1972 in German	R. Hoffmann, R. B. Woodward, "Das Konzept von der Erhaltung der Orbitalsymmetrie," *Chemie in unserer Zeit* **1972**, *6*, 167–174.
W–H 13b	Published in 1973 in Swedish	R. Hoffmann, R. B. Woodward, "Den reaktionskontrollerande orbitalsymmetrin," *Kemisk Tidskrift.* **1973**, *85*, 28–30, 33–34, 37.
W–H 14	Lecture given on August 28, 1973 Published in 2001	R. B. Woodward, "The Arthur C. Cope Award Lecture," In *Robert Burns Woodward. Architect and Artist in the World of Molecules*, (Eds.: O. T. Benfey, P. J. T. Morris), Chapter IV, Chemical Heritage Foundation, Philadelphia, PA, **2001**.

within a very narrow focus,[14–17] that being on their interactions during the research and writing of their first five communications, all published within an eight-month period in 1965.

One goal of this publication is to provide an analysis of the character and indwelling spirit of the Woodward-Hoffmann collaboration as their ideas matured and their publications were beginning to precipitate a revolution in chemistry.[9,18]

Please join in the revelations regarding Woodward and Hoffmann's next several years together (late 1965 to 1967). We shall examine and analyze Woodward and Hoffmann's two unpublished manuscripts and two publications from what we consider their "intermediate years," or what I refer to in Table 1 as the "treading-water publications." Those fall between their first five "core" communications and their last flowering, amplifications of the reach of orbital symmetry control and their pronouncements of the W–H rules. I refer to these as Woodward and Hoffmann's "heart and soul" publications.

2. W-H 1 to W-H 5: A Quick Look Back to 1965

Author's Note: This section provides a short summary of the Woodward-Hoffmann collaboration up to late 1965, during which they published their core publications (W-H 1 – W-H 5). For those readers who are well aware of the history of these publications, especially as told in the previous publications in this series,[15–17,19,20] *please jump directly to Section 3.*

As discussed in detail in previous publications in this series,[21–27] Woodward and Hoffmann arrived on the scene in January 1965 with organic chemistry in a crisis. The mechanism of cyclic concerted valence isomerizations – now known as pericyclic reactions – was so unknown that William von E. Doering had labelled them "no-mechanism" reactions.[28–30] Of course, as Doering knew quite well, all reactions *have* mechanisms. This was his tongue-in-cheek reference to a major chemical mystery of the day.[22,28,29] By way of background:

- We know little as to the first interaction between Woodward and Hoffmann.[31–33] Page 80 of Hoffmann's *Laboratory Notebook 13* is dated May 5, 1964, with the inscription "Talk with Woodward & Applequist."[34] On that page, Hoffmann recorded the alternating thermal and photochemical stereospecific reactions of appropriately substituted 1,3-butadiene ⇋cyclobutene and 1,3,5-hexatriene ⇋ 1,3= cyclohexadiene. Hoffmann immediately performed a series of extended Hückel theory (eHT) calculations that mirrored the experimental results of these electrocyclizations. Woodward wrote a draft.[14] Hoffmann wrote a draft.[14] Woodward pasted these two drafts together and thus became the first W–H publication (submitted on November 30, 1964; published January 20, 1965).[3]
- In late 1964, Hoffmann derived the correlation diagram for the [4+2] Diels-Alder reaction. Early in February 1965, Hoffmann derived the correlation diagram for the [2+2] dimerization of ethene. He then rederived the correlation diagram for the [4+2] reaction of ethene and 1,3-butadiene. Hoffmann immediately observed a difference between these two correlation diagrams. In the [2+2] correlation diagram, there were MO energy level crossings, i.e., bonding MO energy levels correlated with antibonding MO levels. Furthermore, he saw that a doubly-occupied MO crossed with an unoccupied MO. He recognized that these were indicators of a high-energy reaction, later termed a W–H forbidden reaction. In the [4+2] correlation diagram, all the bonding MOs of the reactants correlated with bonding MOs of the products (and of course, the converse). There was no MO energy level crossing of a filled and an unfilled level. Hoffmann understood that this was a characteristic of a low-energy reaction, later termed a W–H allowed reaction. In just these few moments of recognition – some would call this a Eureka moment[35] – Hoffmann identified the cycloaddition mechanism problem and solved it! We can point to the exact laboratory notebook page that of this intellectual gap-jump. Those observations formed the basis of the second W–H *JACS* communication on cycloadditions (submitted on March 22, 1965; published on May 5, 1965). That story is told in a previous publication in this series.[15]
- Immediately after solving the cycloaddition problem, Hoffmann constructed the correlation diagrams for the chair and boat orientations of the Cope reaction (early February 1965). These two correlation diagrams were identical, and both were low-energy reactions. There followed ca. 10 days during which he distinguished between the chair and boat mechanisms for the Cope reaction and also studied cycloadditions of systems beyond [2+2] and [4+2] electron counts.
- Hoffmann then moved on to study numerous miscellaneous reactions. Among those, he derived interaction diagrams coupled with qualitative perturbation theory to analyze [1,*j*] hydrogen migrations and [3,3], [3,5], and [5,5] carbon migrations – all later understood to be of the same reaction type, namely sigmatropic reactions. He began to see alternations in the stereochemistry in these migrations and could distinguish between low energy and high energy TSs in these reactions. He used five different MO tools, including three-center bonding models to support his tentative mechanistic conclusions (end of February to mid-April 1965). Hoffmann provided Woodward with a draft of the sigmatropic reactions communication (W–H 3) which, after upgrading by Woodward, was submitted (April 30, 1965) and published (June 5, 1965). That story is told in a previous publication in this series.[15]
- In the midst of solving the sigmatropic reaction mechanism puzzle, Hoffmann solved the *exo versus endo* Diels-Alder puzzle (the third week of March 1965) *before* he determined the mechanism of sigmatropic reactions (the second week of April 1965).
- In late May or early June 1965, just before leaving Harvard for Cornell University, Hoffmann provided a draft

manuscript to Woodward that combined his Cope SOI mechanism and his Alder *exo-endo* SOI mechanism. On August 4, 1965, Woodward responded, by sending two draft communications to Hoffmann who was then at Cornell – one on the Cope reaction and one on the Alder *exo-endo* mechanism. Woodward essentially had divided Hoffmann's draft into two. One half would become the fourth Woodward-Hoffmann *JACS* communication, the other half would become the fifth. They were both submitted on August 16, 1965, accepted immediately without peer review, and published in the October 5, 1965, issue of *JACS.* The stories behind those two publications – SOIs and the Diels-Alder and the Cope reactions – are recounted in the previous publication in this series.[17]

With these five *JACS* communications,[3–7] Woodward and Hoffmann had made their mark on chemistry. They received quite laudatory praise from the organic chemistry community and from Marshall Gates at *JACS.* Lecture invitations were received by Woodward and Hoffmann. For example, almost immediately after the first W–H was published, Woodward was invited to lecture at the 1966 Bürgenstock Conference on Stereochemistry on May 13, 1966, and at a special symposium held by the Royal Society of Chemistry in Sheffield, England, on July 8, 1966. Of course, Woodward continued his many other research programs, the most visible and consequential being the total synthesis of vitamin B_{12}, performed in collaboration with Albert Eschenmoser and his group at the ETH Zürich (Eidgenössische Technische Hochschule Zürich).[36–44] In between these years was Woodward's receipt of the 1965 Nobel Prize in Chemistry. This event, long overdue,[45] undoubtedly carried with it a set of unique distractions.[46]

Hoffmann was busy as well, developing his own independent research program at Cornell, where he arrived in mid-June 1965. Hoffmann had six publications in 1965, the five communications with Woodward and *Some Theoretical Observations on Cyclopropane*[47] in *Tetrahedron Letters* – a short essay regarding bonding in cyclopropane based on Hoffmann's extended Hückel theory calculations. In 1966, Hoffmann had four publications, three based on eHT calculations and MO perturbation theory conducted at Harvard[48–50] and one published in February 1966 based on a lecture he gave at the New York Academy of Sciences[51] discussed below.

Marshall Gates could not have anticipated how very right he had been in accepting and immediately publishing the W–H communications. A revolution in chemistry had been precipitated.[9] Graduate students around the world were presenting the W–H rules in group meetings, not without some hard-earned educational gain to them and their audiences. There was surely an uptick in the sales of John D. Roberts's[52] and Andrew Streitwieser's[53] 1961 textbooks on MO theory and organic chemistry. And the orbitals of allyl radical, 1,3-butadiene, and 1,3,5-hexatriene were no longer only in the hands of physical and theoretical chemists. Theoreticians found different ways to derive the Woodward-Hoffmann rules.[54–59] Woodward and Hoffmann continued to receive a plethora of lecture invitations. And in due course, the 1981 Nobel Prize in Chemistry would honor the W–H rules.

3. Invitation from the Editor of *Angewandte Chemie* to Write "a Somewhat More Elaborate Review"

On July 1, 1965, shortly *after* Woodward and Hoffmann published their third 1965 *JACS* communication[5] on sigmatropic reactions (Table 1) and shortly *after* Hoffmann arrived in Ithaca as an untenured associate professor, Woodward received an invitation from Germany. Helmut Grünewald, the editor in chief of *Angewandte Chemie*, and his assistant G. Kruse, wrote:

"Your communication on the 'Stereochemistry of Electrocyclizations' seems to be so much of general interest that we wish to invite you and Dr. Hoffmann to write a somewhat longer review on the same subject … "[60]

Notably, Grünewald and Kruse did not mention Woodward and Hoffmann's second and third *JACS* communications. On September 29, 1965, Woodward responded to Grünewald in the mildly affirmative:

"It does seem that these developments are of general interest and applicability over a wide area of organic chemistry, and I agree that Angewandte Chemie would be an outstanding vehicle for their presentation in a useful and effective way. Consequently, I should like to accept your invitation, but my very many commitments in writing and other directions do not permit me to foresee a definite period in which I might be able to find the time to prepare an appropriate manuscript. In these circumstances, may I leave it that I shall be glad to get in touch with you again at some time in the future if I can find and seize such an opportunity … to prepare an appropriate manuscript."[61]

Woodward immediately moved on to other more pressing matters. He certainly recognized that *Angewandte Chemie* was a resurgent and prominent international journal. Woodward was already basking in the glory of being the most prominent organic chemist in the world,[62] a rock star in his own community,[63–67] the Pope of Chemistry.[68] And just a few weeks later, he would receive the call for that year's Nobel Prize in Chemistry. *Angewandte Chemie* would just have to wait until a more propitious time. Its time would come, prompted by a manuscript drafted by Hoffmann and new research results also provided by Hoffmann. This story will be told in the next publication in this series.[69]

4. W-H 6NP: Woodward and Hoffmann's Sixth 1965 Communication – Never Submitted, Never Published[70]

On August 15, 1965, just as Woodward was submitting the fourth and fifth Woodward-Hoffmann communications to *JACS*,[6,7,17] Hoffmann mailed to Woodward a manuscript intended to be their sixth *JACS* communication. This manuscript was entitled "Some Further Selection Rules for Cycloadditions."[70] Hoffmann wrote,

> "I have written up and attached a version of still another paper which I think takes care of the remnant of the significant work we did this spring … Let me know your opinion of the material. With best regards, Roald"[71]

The content of this manuscript is encapsulated by Figure 1(top), which contains six graphical excerpts from Hoffmann's draft. Included in the draft were several new reaction types not discussed in previous W–H publications, these being cheletropic reactions, group transfers and eliminations.

Another excerpt from Hoffmann's cover letter to Woodward is interesting. Hoffmann wrote:

> "The right-hand side of drawing **Vib** [see Figure 1] was put in for illustrative purposes only and perhaps is not needed. Actually [Hoffmann's Cornell colleague and former Woodward graduate student] Jerry Meinwald and I have thought of some plausible syntheses of the interesting tetraene and, unless you have someone working on it, will go ahead and put someone to make it. Perhaps that would be still another reason to omit this scheme from the drawing."[70]

Clearly, Hoffmann was hungry to publish and to push the frontiers of chemistry – and push Woodward. As Hoffmann readily acknowledged,

> "I had no hesitation in suggesting to Woodward what might be a good thing to do."[2]

In 1964 and 1965, Hoffmann continued to advance his research unrelated to the W–H collaboration and pericyclic reactions. Four days after sending Woodward the intended sixth W–H communication (W–H 6NP), on August 19, 1965, Hoffmann wrote another short note to Woodward (Figure 2) in which he enclosed two additional manuscripts he had just completed. One of these was co-authored by Roy A. Olofson, another former graduate student of Woodward's[73–77] who had stayed at Harvard for several years (1961–1965), first as an instructor, then assistant professor. The Hoffmann – Olofson manuscript reported the use of eHT calculations and qualitative perturbation theory that explored the relative stabilities of various radicals and anions of allyl systems. Based on Hoffmann's list of publications and dates of submission (see the caption in Figure 2), the second was likely "Some Theoretical Observations on Cyclopropane" published in *Tetrahedron* Letters.[47] Hoffmann was certainly plunging into the application of MO theory in organic chemistry, with Woodward and other collaborators and on his very own. We do not know to what extent Woodward was aware of Hoffmann's collaboration with Olofson. Judging from this letter, Hoffmann did not seem to feel he had to clear the topics of his research with Woodward.

Back to Woodward and Hoffmann's sixth *JACS* communication. Not hearing from Woodward on his W–H draft – not an unusual consequence of writing to Woodward who was, even by his own admission, a tardy correspondent[66,79] – Hoffmann, within his usual alacrity, moved forward on the manuscript. On September 24, 1965, Hoffmann sent an updated draft[80] with the same title to Woodward.[81] Hoffmann wrote, "Here's a new version of the 6th communication."[81] Still receiving no response from Woodward, Hoffmann found a happy opportunity to write another reminder to him (Figure 3). Yes, indeed, a third request for Woodward's review of a manuscript draft written by Hoffmann with Woodward's name listed as a co-author! On October 11, 1965, Hoffmann sent a congratulatory note to Woodward on the announcement of his Nobel Prize. But being quite upfront with Woodward, Hoffmann used the opportunity to encourage Woodward on their sixth communication: "I hope that the added burden in these days will not prevent you from getting the 6th communication in shape."[82] Hoffmann never did receive a written response from Woodward.[83] Perhaps he nonetheless knew Woodward's response.

In 2017, Hoffmann recalled,

> "I didn't even remember that I ever wrote this draft! It was not published, obviously. Nor submitted, as far as I know. But … some of the ideas came into focus in a long 1971 paper[72] with Mel Goldstein."[84]

Hoffmann did live up to his self-description of being a salvager. Woodward's silence notwithstanding, Hoffmann would include structures **I–VI** of Figure 1 in his soon-to-be-submitted, sole-authored publication in the *New York Academy of Sciences* journal (Section 5).

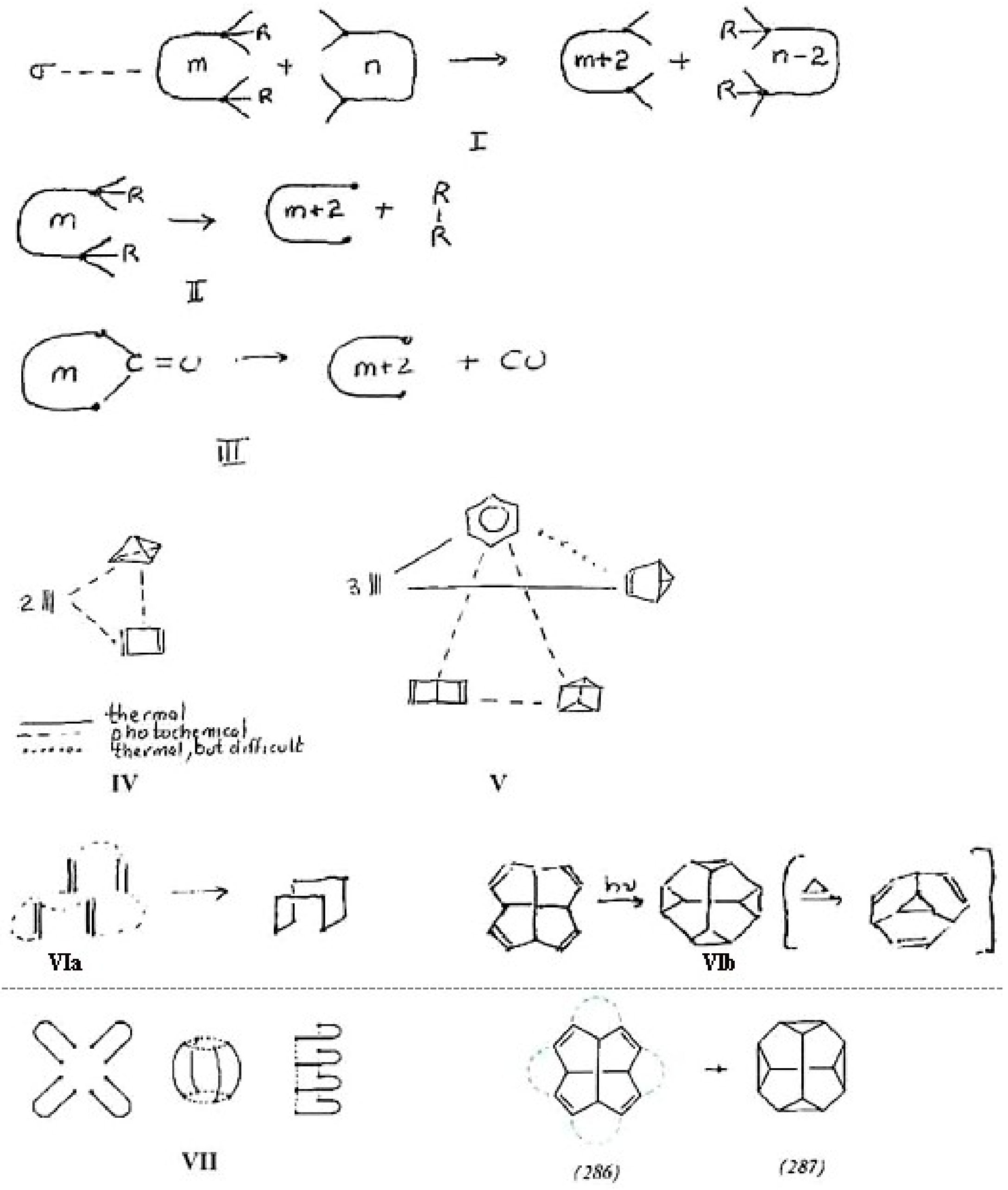
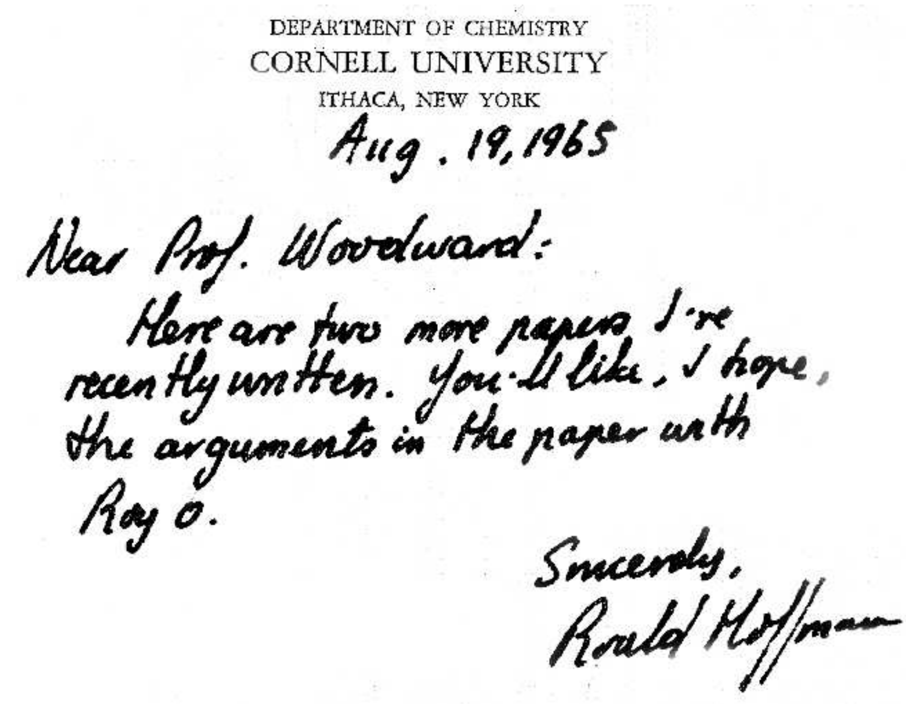


Figure 1. (Top) Graphics **I–VI** are reproduced from Hoffmann's first draft[70] of a manuscript entitled "Some Further Selection Rules for Cycloadditions" which was intended by him to be the sixth W–H communication of 1965. The manuscript, as such, was never submitted for publication. (Bottom) Hoffmann was not going to waste his ideas or his writings. Being a "salvager," Hoffmann was able to use most of the chemistry including that shown in the (Top) in later articles. For example, the three structures shown as **VII** are derived from **VIa** and appeared in Hoffmann's 1971 *JACS* publication with his Cornell colleague Melvin J. Goldstein entitled "Symmetry, Topology, and Aromaticity."[72] Structures **286** and **287** appeared in W–H's 1969 treatise[12] and 1970 monograph[13]; compare these with structures shown by **VIb**.



DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

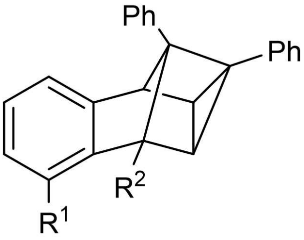
Aug. 19, 1965

Dear Prof. Woodward:

Here are two more papers I've recently written. You'll like, I hope, the arguments in the paper with Roy O.

Sincerely,
Roald Hoffmann

Figure 2. Hoffmann's cover letter to Woodward on August 19, 1965, in which he provided Woodward with two "recently written"[78] manuscripts, one with Roy Olofson on "The Dependence of Conformational and Isomer Stability on the Number of Electrons in Extended π Systems,"[50] submitted to *JACS* on September 21, 1965. The other is likely to have been "Some Theoretical Observations on Cyclopropane,"[47] submitted to *JACS* on August 21, 1965. It is amusing to note that Hoffmann signed his letter "Roald Hoffmann," this after Woodward and he had already published three breakthrough *JACS* communications and had submitted two others. Furthermore, how many individuals named "Roald" might Woodward have known, for Hoffmann to include his last name, especially those having Hoffmann's trademark penmanship?



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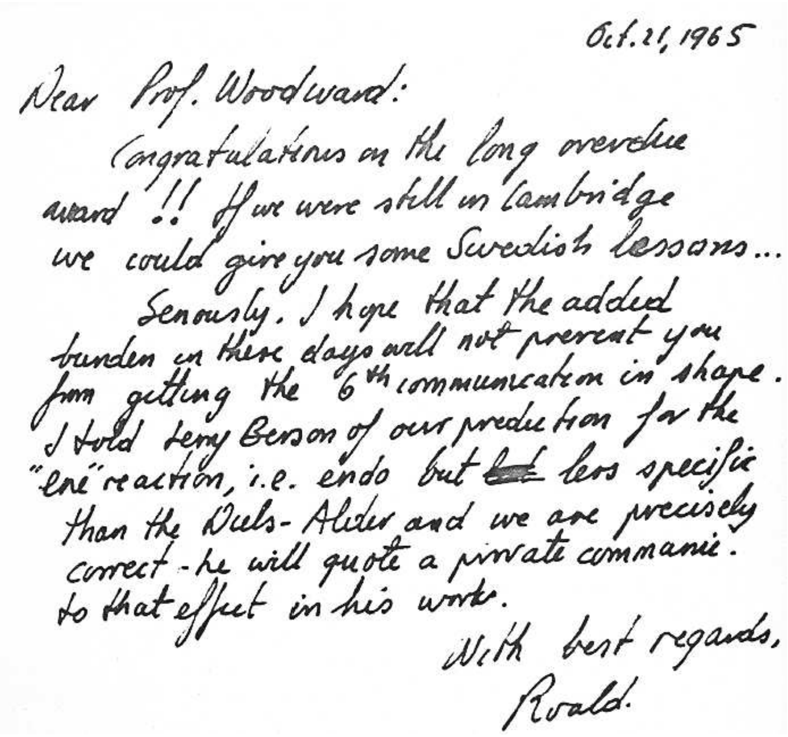
I asked of Hoffmann, "Given the instantaneous acceptance of the first five papers, please tell me why this sixth manuscript was not submitted to JACS." He responded:

"I don't know. Probably we thought the long paper [the term later frequently used by Hoffmann for the 1969 *Angewandte Chemie* treatise[12,13]] was imminent (instead of taking four years) and decided to save it for that. Anyway, the decisions on publications were still mostly Woodward's at that time."[85]

It is true that Hoffmann never received an updated draft from Woodward nor a hint from him that an updated draft would one day be received.[83] Hoffmann cannot recall receiving any written (or oral) response from Woodward.[86] Remember, that is the procedure that Woodward used in the previous five W–H communications in *JACS*.[3–7] He would receive a draft from Hoffmann, then he would incorporate his changes and provide a near final draft to Hoffmann.[14–16] Even in the case of the fourth[6] and fifth[7] W–H communications, Woodward divided a Hoffmann draft into two manuscripts and returned two finalized manuscripts to Hoffmann for his approval.[17] But as it turn out, there is evidence that Woodward examined Hoffmann's draft(s).

Within the Woodward papers at the Harvard Archives is one of Hoffmann's drafts of W–H 6NP in which some of Woodward's handwritten notes appear (Figure 4). True, these notes are minimal. While hard to read, on page 5 of the manuscript, Woodward appears to have written the names of four chemists: Petite and Masamune on the left, below the structure of cyclobutadiene; and Viene and Sasse on right, below the structure of prismane. Roland Petite and Satoru Masamune published important research on cyclobutadiene derivatives.[87,88] Wolfgang H. F. Sasse published on prismane-



Oct. 21, 1965

Dear Prof. Woodward:

Congratulations on the long overdue award !! If we were still in Cambridge we could give you some Swedish lessons...

Seriously, I hope that the added burden in these days will not prevent you from getting the 6th communication in shape. I told Jerry Berson of our prediction for the "ene" reaction, i.e. endo but ~~but~~ less specific than the Diels-Alder and we are precisely correct - he will quote a private communic. to that effect in his work.

With best regards,
Roald.

Figure 3. Hoffmann's letter to Woodward dated October 21, 1965.[82] In this letter, Hoffmann congratulated Woodward on his upcoming Nobel Prize and joked with him about teaching Woodward Swedish (as Hoffmann's wife, Eva, is Swedish by birth, and he had become fluent in Swedish by then). Hoffmann also inquired hopefully about the fate of the draft of their sixth (never published) communication that he had sent to Woodward previously.

like structures, e.g., **1**,[89] and one of the earliest chemists to explore strained ring compounds prepared photochemically as energy sinks-energy sources. I was unable to find a "Viene" that matched the occasion.

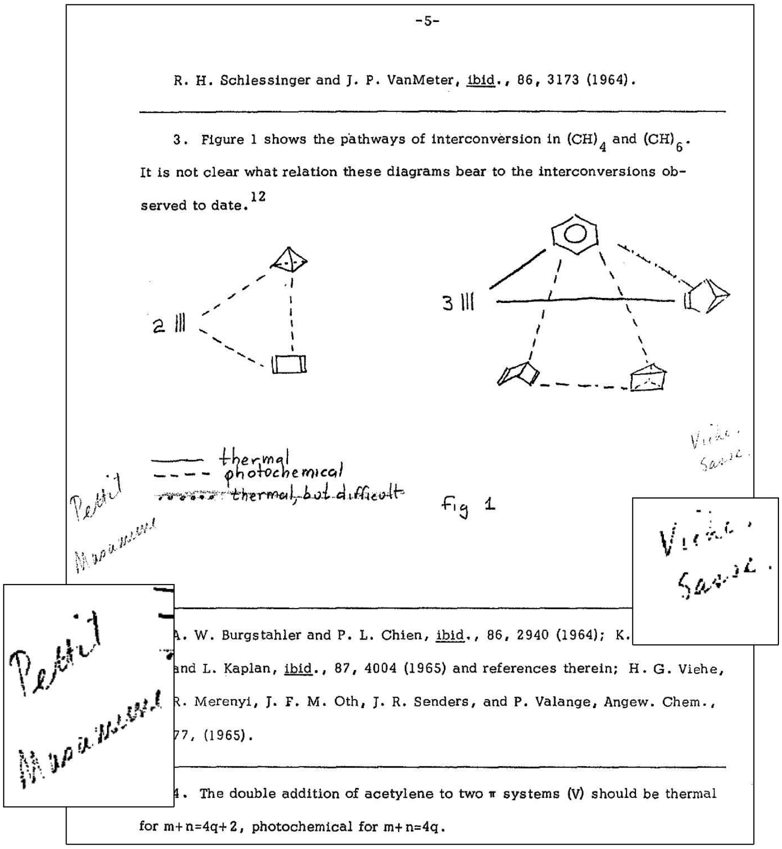
5. W-H 7: *Transactions of the New York Academy of Sciences* (1966): "The Electronic Structure of Some Intermediates and Transition States in Organic Reactions"[51]

On January 4, 1966, Hoffmann lectured at a meeting of the New York Academy of Sciences in New York City on "The Electronic Structure of Some Intermediates and Transition States in Organic Reactions." This was one of many invitations Hoffmann received after the publication of the W–H rules. (As his mother and stepfather lived in New York City, he was unlikely to refuse an invitation to visit the Big Apple.) As was the custom of the Academy at that time, lecturers were asked to publish an article in their major publication based on that lecture. The publication's title[51] matched the title of Hoffmann's lecture. Hoffmann was the sole author of W–H 7. Nonetheless, the first sentence in the second paragraph of this publication reads,

"In collaboration with R. B. Woodward at Harvard, we have used a similar approach ['correlation diagram[s]'] for the study of concerted reactions."[51]

The *Transactions of the New York Academy of Sciences* was a first-class journal published from 1881 to 1983. This journal's quality is quickly revealed by considering the chemists who published articles in its "Section of Chemical Sciences" for Volume 28 (the 1965–1966 academic year; Table 2). Of this group, three would become members of the U.S. National Academy of Sciences. While Hoffmann was the most newly-minted Ph.D., to some extent, his unnamed co-authors were that year's Nobelist Woodward and Olofson who had just assumed his faculty position at Pennsylvania State University.

Figure 5 reproduces an excerpt from the second page of this publication. Here Hoffmann presented several key reaction types, expanding the scope of cyclic concerted reactions whose orbital symmetry mechanisms had up to that moment, not yet been explained by Woodward and Hoffmann. It is evident from Figure 3 that many new chemical analyses were reported in that quite concise publication. That the actual chemical reactions presented were well known in not the point.



-5-

R. H. Schlessinger and J. P. VanMeter, ibid., 86, 3173 (1964).

3. Figure 1 shows the pathways of interconversion in $(CH)_4$ and $(CH)_6$. It is not clear what relation these diagrams bear to the interconversions observed to date.[12]

Pettit

Masamune

Viehe.
Sauer.

A. W. Burgstahler and P. L. Chien, ibid., 86, 2940 (1964); K. and L. Kaplan, ibid., 87, 4004 (1965) and references therein; H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders, and P. Valange, Angew. Chem., 77, (1965).

4. The double addition of acetylene to two π systems (V) should be thermal for $m+n=4q+2$, photochemical for $m+n=4q$.

Figure 4. Page 5 from a draft manuscript of W-H 6NP written by Hoffmann[90] and provided to Woodward. On this page, Woodward made note[80] of several chemists whose research related to Hoffmann's text, likely as pointers to possible citations. The only other handwritten marks in the draft was a reference on page 3, not shown in this publication.

It was an easy publication for Hoffmann to write, given that he had written much of the chemistry in his draft *JACS* communication (W–H 6NP),[70] some four months earlier and lay unused (Section 3). Hoffmann-the-salvager rescued the chemistry from that abandoned, castaway manuscript and found a way to publish the material almost immediately thereafter. The handwritten drawings are clearly by Hoffmann; he could not yet afford to hire a draftsperson who would manually draw them using India ink and stencils, as was done in the 1960s and for many years to come.

I asked Hoffmann, "Why was Woodward not a co-author of your *Transactions of the New York Academy of Sciences* publication[51]? He responded:

"I don't know. I presume that this was just a talk I gave, and neither I nor Woodward took the publication of it seriously."[103]

The fact that Woodward was not a co-author of Hoffmann's *Transactions* publication followed the practice within the chemistry community in the 1960s and for many years thereafter: generally, only the lecturer was the author of publications that stemmed directly from invited lectureships. Even though these were singly-authored publications, everyone knew that the actual hands-on labor, and some, if not many or even most, of the intellectual contributions were performed by the professors' students. But this was a turn-about, in that Hoffmann was junior to Woodward in terms of professional status – but an equal, perhaps more than an equal, in their collaboration. And turnabout was fair play. Hoffmann was not a coauthor of Woodward's Royal Society Lecture entitled "The Conservation of Orbital Symmetry" that was presented in 1966 and published in 1967[104] (W–H 9). We will come to that publication in the next section.

As to "taking the publication seriously,"[103] Hoffmann's view – which may not have been shared by Woodward, if Woodward even knew about the lecture and the publication – is consistent with Hoffmann's attitude toward preliminary disclosure of his research results. Hoffmann's publication in the *Transactions of the New York Academy of Sciences*[51] revealed

Table 2. Chemistry presentations at the New York Academy of Sciences and publications in volume 28 of the *Transactions of the New York Academy of Sciences.*

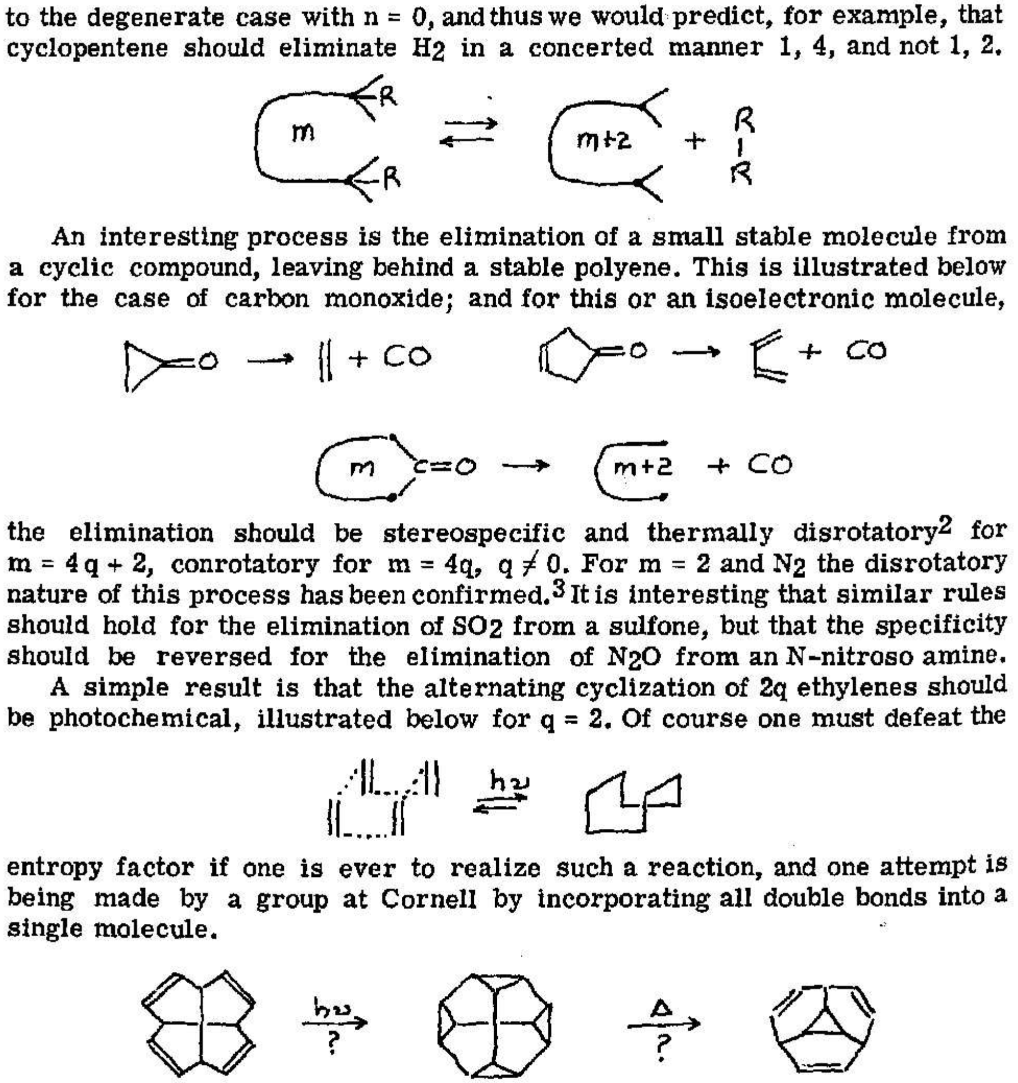
Author	Author's location	Lecture and publication title	Date of presentation
George deStevens[91]	Ciba-Geigy Pharmaceutical Company, later a member of the Charles A. Dana Research Institute for Scientists	"New Heterocyclic Systems"[92]	February 3, 1965
Leo A. Paquette[93]	Ohio State University	"Unsaturated, Medium-sized, Heterocyclic Rings: Synthesis and Selected Reactions"[94]	December 7, 1965
Roald Hoffmann	Cornell University	"The Electronic Structure of Some Intermediates and Transition States in Organic Reactions"[51]	January 4, 1966
Charles H. DePuy[95]	University of Colorado	"Cyclopropanols: Synthesis and Electrophilic Ring-Opening"[96]	February 1, 1966
Arnold Brossi[97]	Hoffmann-La Roche	"New Approaches on the Synthesis of Isoquinoline Derivatives Related with Natural Products"[98]	March 1, 1966
Eugen Müller[99]	University of Tübingen	"Approaches to Cyclobutadiene"[100]	April 5, 1966
Andrew S. Kende[101]	Lederle Laboratories, American Cyanamid, later s faculty member of the University of Rochester	"Recent Chemistry of Methylenecyclopropene Systems"[102]	May 3, 1966

several new reaction types that were governed by the orbital symmetry selection rules. Other chemists were already studying that chemistry. Two of them can be readily identified, both of whom had private correspondence with Hoffmann on the theme in 1965 and 1966. One was John E. Baldwin[105–108] who was then at the University of Illinois, later at the University of Oregon and ultimately at Syracuse. The other was David M. Lemal[109–111] at Dartmouth.

Might Hoffmann's ideas be 'scooped' by his preliminary announcements or by his private correspondence with two potential competitors? It appears that Hoffmann did not concern himself about such matters, nor did Baldwin and Lemal. For example, at the October 1964 Natick Conference on Organic Chemistry, without consulting Woodward to obtain his agreement if not approval, Hoffmann gave an impromptu mini-talk in which he revealed *for the very first time*, the orbital symmetry mechanism of electrocyclizations.[14,112] Yes, this was before he and Woodward even began to write their first communication. As Hoffmann recently summarized,

> "I was never concerned, then and later, about whether to talk or write about any subject. Could that be because I was operating on a naïve view of science as a gift economy? That I never did anything that could be patentable?"[113]

There are other considerations regarding authorship, credit, and intellectual property priority. Only a portion, approximately 50 %, of Hoffmann's *Transactions* publication involves pericyclic reactions and the concept of orbital symmetry control. And of that 50 %, while that material rests firmly within the boundaries of pericyclic reactions, Hoffmann's laboratory notebooks clearly show that the reactions and ideas in Figure 5 derived from Hoffmann's side of the ledger, not Woodward's. The rest of Hoffmann's *Academy* publication deals with theoretical research that Hoffmann conducted with Olofson. The results with Olofson had already been submitted to *JACS* for publication on September 21, 1965, and published[50] in the March 5, 1966, issue of that journal. Furthermore, the majority of the research and the entire drafting of the submission were performed by Hoffmann. There is no evidence that either Woodward or Olofson sought co-authorship or were offended that they were not offered co-authorship.



to the degenerate case with n = 0, and thus we would predict, for example, that cyclopentene should eliminate H_2 in a concerted manner 1, 4, and not 1, 2.

An interesting process is the elimination of a small stable molecule from a cyclic compound, leaving behind a stable polyene. This is illustrated below for the case of carbon monoxide; and for this or an isoelectronic molecule,

the elimination should be stereospecific and thermally disrotatory[2] for $m = 4q + 2$, conrotatory for $m = 4q$, $q \neq 0$. For $m = 2$ and N_2 the disrotatory nature of this process has been confirmed.[3] It is interesting that similar rules should hold for the elimination of SO_2 from a sulfone, but that the specificity should be reversed for the elimination of N_2O from an N-nitroso amine.

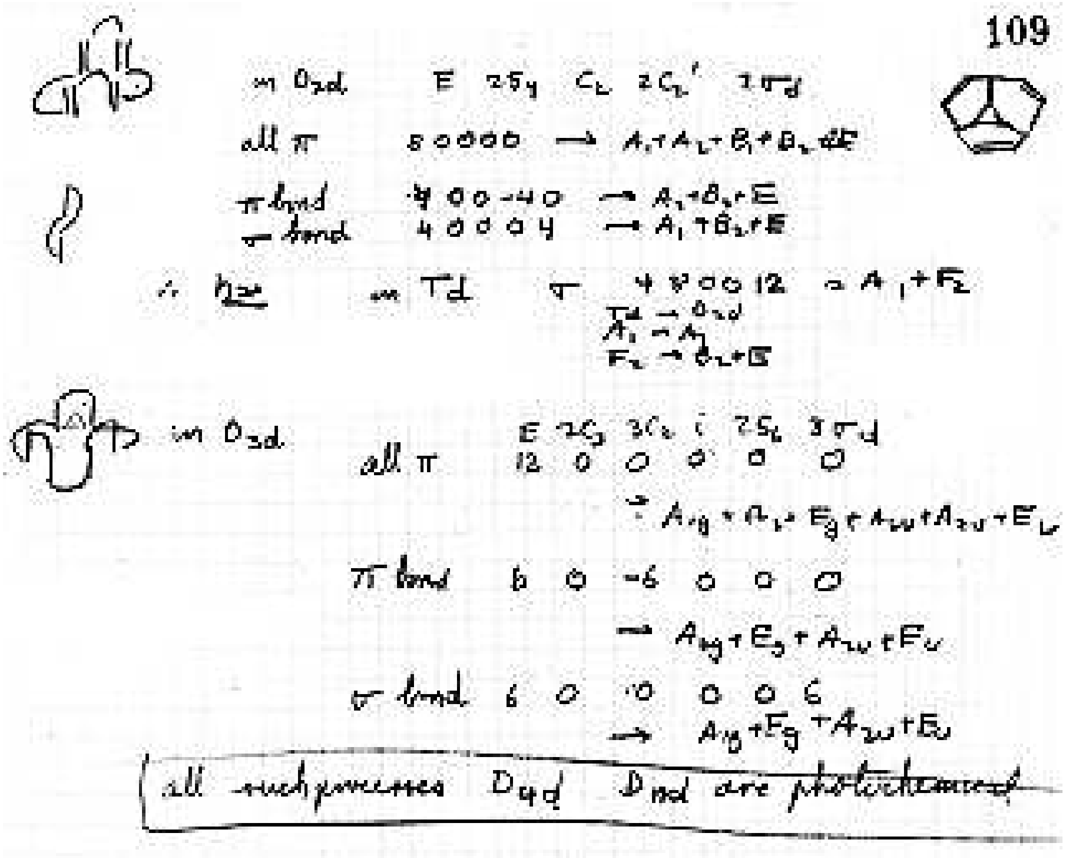
A simple result is that the alternating cyclization of 2q ethylenes should be photochemical, illustrated below for $q = 2$. Of course one must defeat the

entropy factor if one is ever to realize such a reaction, and one attempt is being made by a group at Cornell by incorporating all double bonds into a single molecule.

Figure 5. Excerpt from page 476 of Hoffmann's 1966 publication in the *Transactions of the New York Academy of Sciences.*[51] This is the sixth Woodward-Hoffmann publication, numbered W–H 7 herein (see Table 1). Compare the structures on this page with those shown in Figure 1. Reprinted with permission from the New York Academy of Sciences.

It is seductive to follow the trail of ideas backwards, from publication to origination. It is the ultimate back story of research. Consider Figure 6 from one of the last notebook pages (*Laboratory Notebook 17*, page 109) composed by Hoffmann at Harvard, his homebase for the previous seven years. (Nostalgia talking.) Figure 6 was written ca. June 1, 1965, just two weeks before he departed Cambridge for Ithaca. We can trace some of the most intriguing ideas from that laboratory notebook page to the unpublished 6th "*JACS*" manuscript (W–H 6NP) and to the *Academy* publication (W–H 7). For example, the structures at the top-left and top-right in Figure 6 appear in the fourth and fifth rows of structures in Figure 1 (W–H 6NP) and in the fourth and fifth rows of Figure 5 (W–H 7).

The group theory shown in Figure 6 would certainly impress most if not all organic chemists, but they were the bread and butter of Hoffmann's Ph.D. education and experience. What is more impressive than this group theory is Hoffmann's imagination within the universe of organic chemistry. Consider his conceptualization of the valence isomerization of the tetraene at the top left Figure 6 to its cycloaddition product at the top right. Is this a chemical reaction that a chemical physicist in 1965 would imagine? Or does it look more like the wild imagination of an organic



109

in D_{2d} E $2S_4$ C_2 $2C_2'$ $2\sigma_d$

all π 8 0 0 0 0 → $A_1+A_2+B_1+B_2+2E$

π bond 4 0 0 -4 0 → A_1+B_2+E

σ bond 4 0 0 0 4 → A_1+B_2+E

∴ hν in T_d σ 4 1 0 0 2 → A_1+F_2

$T_d \rightarrow D_{2d}$

$A_1 \rightarrow A_1$

$F_2 \rightarrow B_2+E$

in D_{3d} E $2C_3$ $3C_2$ i $2S_6$ $3\sigma_d$

all π 12 0 0 0 0 0

→ $A_{1g}+A_{2g}+E_g+A_{1u}+A_{2u}+E_u$

π bond 6 0 -6 0 0 0

→ $A_{1g}+E_g+A_{2u}+E_u$

σ bond 6 0 0 0 0 6

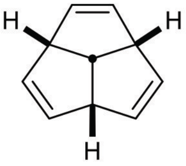
→ $A_{1g}+E_g+A_{2u}+E_u$

(all such processes D_{4d} D_{nd} are photochemical

Figure 6. An excerpt from page 109 of Hoffmann's *Laboratory Notebook 17*, ca. June 1, 1965. Notice Hoffmann's extensive use of symmetry and group theory to predict the reactivity of some of these molecules. The structures at the left and top right appear in W–H 6NP in Figure 1 (structure VI) and Figure 5 (bottom).

chemist? And how many organic chemists would imagine this transformation? As Hoffmann summarized in February 2025,

"The three reactions at the left column [of Figure 6] contain four or two or three double bonds "standing vertically," set up for all antarafacial [2+2+2+2], [2+2], and [2+2+2] cycloadditions. If you build models, you will see these. The triquinacene-like molecule at top right obviously is NOT set up for an all-antarafacial cyclization, but for an all-suprafacial one, which is allowed, but as far as I know, it is not known."[114]



Triquinacene

Perhaps had interest in triquinacene-like compounds given that Woodward et. al. had just recently reported the synthesis of its C_{10}-parent.[115]

6. W-H 8NP: "A Catalogue of Concerted Reactions"[116]

a. Woodward's and Hoffmann's Penchant for Organization and Generalization

From very early in his career, Woodward liked generalizations and rules relating spectroscopic properties to structure. Woodward had the ability to take many facts and organize them in such a way that explanations and predictions could be made and used far and wide, i. e., that they be portable.[117–119] It is also interesting that Woodward liked "rules," as he was quite against rules that governed his personal and professional lives.[64,66,120]

Woodward proposed his first set of rules in the early 1940s when he was in his mid-20s. These are today known as Woodward's UV rules[121] and relate the structure of 1,3-dienes and α,β-unsaturated ketones to the position of their UV absorption maxima.[122–125] These UV rules were developed to assist in structure determinations at a time when other tools had yet to be invented, e.g., NMR spectroscopy, mass spectroscopy, not even X-ray crystallography. His second set of rules were published with William Moffitt, Albert Moscowitz, William Klyne, and Carl Djerassi in 1961. These authors proposed the Octant Rule to predict the absolute configuration of chiral ketones by way of the sign of their Cotton Effect.[126] The third set of rules were, of course, the Woodward-Hoffmann rules.

"Rules" require a large assemblage of data upon which they are derived. Hoffmann began early in his collaboration with Woodward to develop selection rules for the various pericyclic reactions, as documented in his laboratory notebooks.[14–17] For example, Figure 7 contains Hoffmann's collection of eight- and 10-electron cycloadditions. Hoffmann drew three correlation diagrams and concluded that, for thermal reactions specified by the "Δ", the [4+4] and [6+2] cycloadditions were high energy reactions (see the MO energy levels crossing the nonbonding region from bonding into antibonding energies). In contrast, the [6+4] correlation diagram was quite different (no MO energy level crossing the nonbonding region); all bonding MOs of the starting material correlate with bonding MOs of the products. The [6+4] cycloaddition was a low energy reaction. The reverse energetics were recorded for the photochemical reactions, i.e., where Hoffmann recorded "hυ" in Figure 7. Without stipulating so, Hoffmann was considering only suprafacial cycloadditions – the distinction with antarafacial cycloadditions was a concept he had not yet considered.

At the bottom left of Figure 7, Hoffmann recorded a very early stage "table" of six-electron, eight-electron, 10-electron, and 12-electron cycloaddition rules. This simple selection rule was derived ca. February 3, 1965. Six weeks later, a much more formalized and complete cycloaddition selection rule was

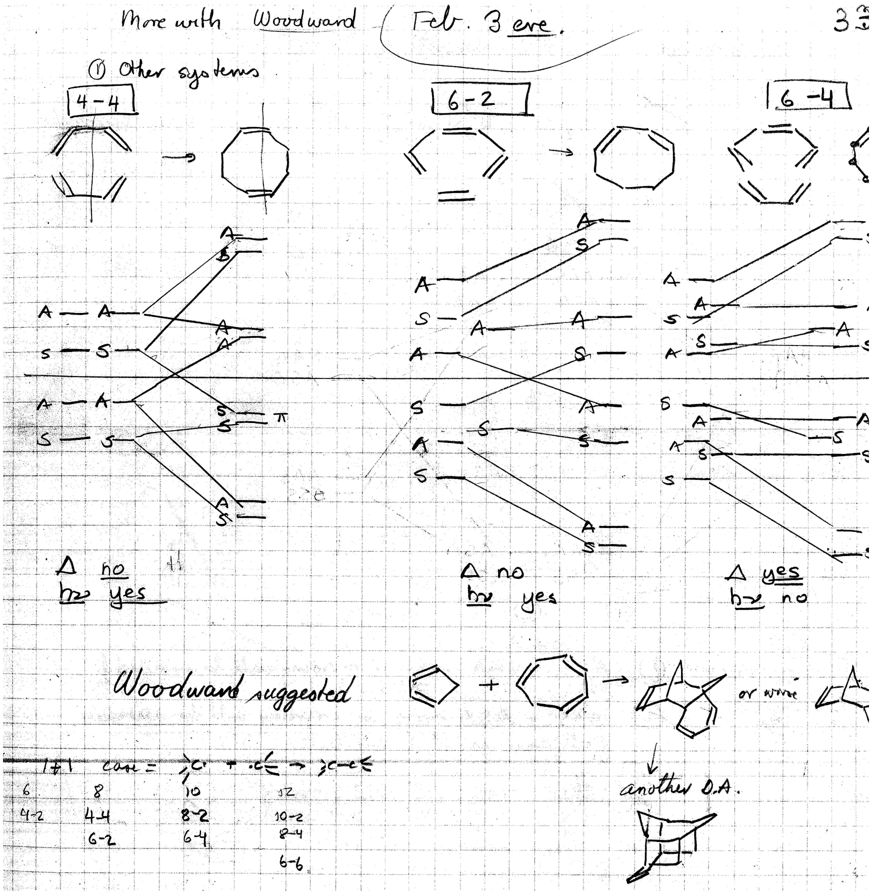


Figure 7. Excerpt from Hoffmann's *Laboratory Notebook 16*, page 33, ca. February 3, 1965. Hoffmann analyzed several eight-electron and 10-electron cycloadditions (top correlation diagrams). At the bottom left, he provided the first steps toward a generalized cycloaddition selection rule that appeared in Woodward and Hoffmann's 1969 treatise.[12] Note the visual similarity for the two correlation diagrams for the eight-electron transformations. And the dramatic difference between the correlation diagrams for the eight-electron (W-H forbidden) *versus* the 10-electron (W-H allowed) transformations.

incorporated in Hoffmann and Woodward's second communication on cycloadditions (W–H 2), submitted on March 22, 1965 (Figure 8).[5]

Figure 8 provides one type of structure-property categorization: that being for cycloadditions, a tabulation of allowed or forbidden reactions by reaction conditions (i. e., thermal or photochemical) and by electron count. On ca. March 14, 1965, Hoffmann drew in his laboratory notebook another type of structure-property categorization: that being all the types of pericyclic reactions for the same electron count. Figure 9 illustrates one of a number of such pages. Notable is the inclusion of many types of pericyclic reactions, e. g., cycloadditions, group transfers and eliminations, and a Cope-like transformation. Stereochemistry is not discussed, and the "no" and "yes" assignments suggest that Hoffmann was only considering suprafacial reactions (though, at that time, the descriptor "suprafacial" had been used only for sigmatropic reactions). Antarafacial cycloadditions were still in the future for Woodward and Hoffmann.

We now jump nine months forward. In a January 11, 1966, letter to John Baldwin, Hoffmann wrote:

"In fact, I think one can now generate selection rules for every reaction in the classification scheme I sent to you (as I thought, it is incomplete. Some additional guesses have brought me to 103 reactions [in the catalogue] through 10 electrons and I'm writing a program to guess them all by computer.)"[127]

Clearly, offmann had generalized Figure 9. How very impressive! A selection rule "for every reaction."[127] Hoffmann was certainly in the mode of generalizations. But what exactly was the "classification scheme" to which Hoffmann had referred? What were those 103 reactions through 10 electrons? We will next see the production of Hoffmann's classification scheme.

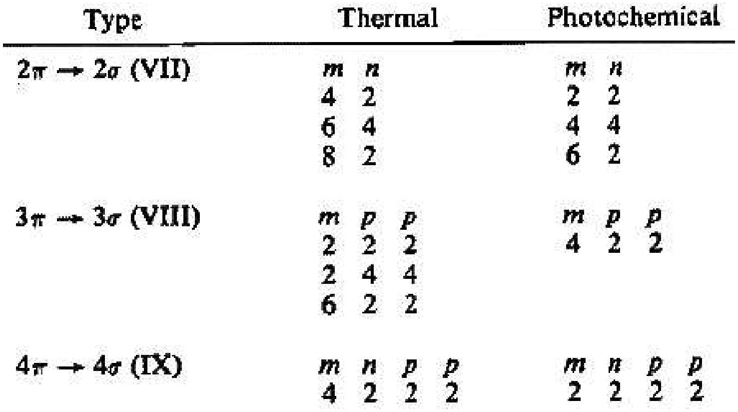
b. The Catalogue

In the summer of 1965, Hoffmann was eager to begin his independent research program at Cornell. Undergraduates served as some of the earliest members of his research group. Almost immediately after his arrival at Cornell in mid-June 1965, Hoffmann began working on "A Catalogue of Concerted Reactions."[116] Indeed, that was the very name he gave to the ultimate result of that work.[116] The development of this catalogue was well within the grasp and capabilities of undergraduates and was low-hanging fruit from their and Hoffmann's perspective. By involving undergraduates in research in chemistry, Hoffmann would simultaneously contribute to the educational responsibilities of university faculty members as well as to his research program.

We know when Hoffmann began working on this "Catalogue" for several reasons. First, two undergraduates date their research with Hoffmann to the summers of 1965 and 1966. Second, Hoffmann sent a copy of the "Catalogue" to Woodward on January 21, 1966[121] (Figure 10). What was this catalogue of concerted reactions? Hoffmann informed Woodward that he had produced "an enumeration of all concerted processes with less than 10 electrons taking place on the periphery of a circle,"[128] i. e., pericyclic reactions.

In Hoffmann's words from the first two drafts of the "Catalogue," he produced

"a systematic enumeration of all reactions of the simplest cyclic topology, i. e., all bond changes taking place on the periphery



Type	Thermal	Photochemical
$2\pi \rightarrow 2\sigma$ (VII)	m n	m n
	4 2	2 2
	6 4	4 4
	8 2	6 2
$3\pi \rightarrow 3\sigma$ (VIII)	m p p	m p p
	2 2 2	4 2 2
	2 4 4	
	6 2 2	
$4\pi \rightarrow 4\sigma$ (IX)	m n p p	m n p p
	4 2 2 2	2 2 2 2

Figure 8. Table 1 from Hoffmann and Woodward's second communication on cycloadditions comprises their selection rule for allowed cycloadditions, submitted on March 22, 1965, and published in the May 5, 1965, issue of *JACS.*[4] At this time, all cycloadditions were considered to be suprafacial, and not because Woodward and Hoffmann had ruled out antarafacial cycloadditions. Rather, they had yet to envision antarafacial cycloadditions that require a very special orientation, i. e., a perpendicular approach of the reactants. Reprinted with permission from R. Hoffmann, R. B. Woodward, *J. Am. Chem. Soc.* **1965**, *87*, 2046-2048. Copyright 1965 American Chemical Society.

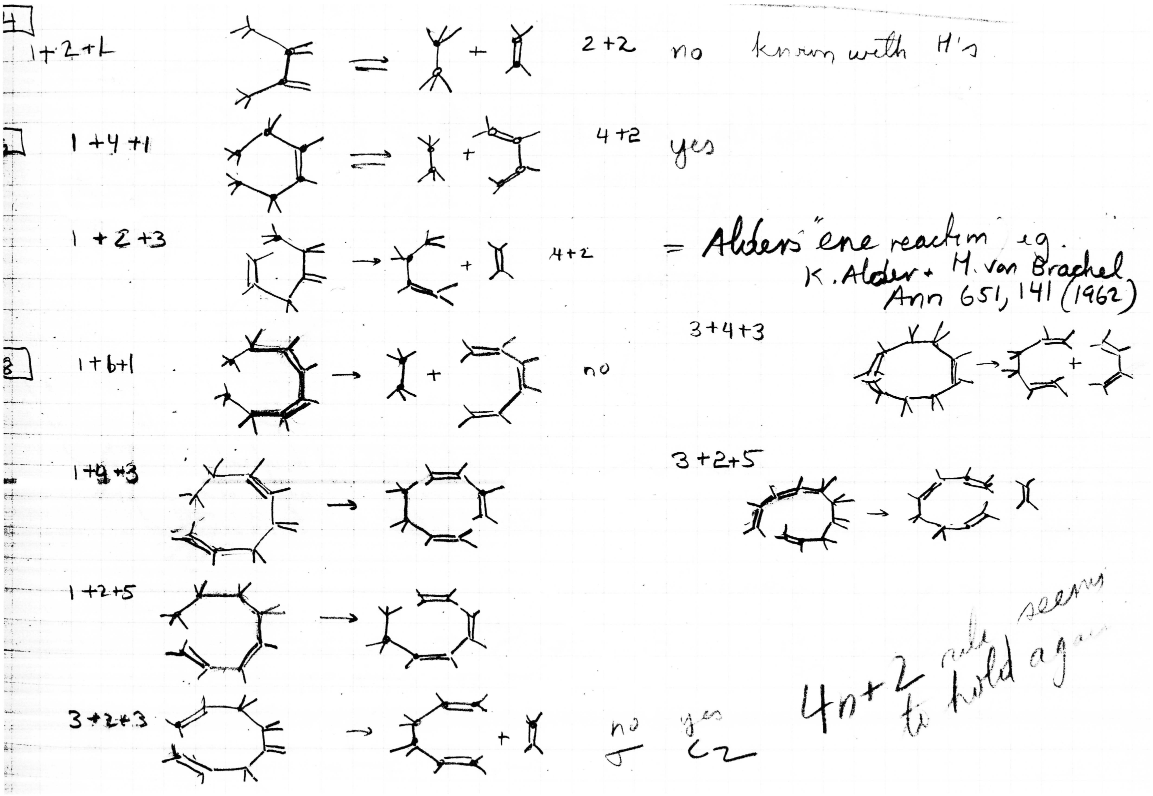


Figure 9. Excerpt from Hoffmann's *Laboratory Notebook 16*, page 143, ca. March 14, 1965. This page records four electron, six electron, and eight electron pericyclic reactions – including group transfers and eliminations, and a Cope-like transformation. Several notations of "2+2 no" and "4+2 yes" led to Hoffmann's statement, the "4 n+2 rule seems to hold again." He did not specify the alternation effect in pericyclic reactions, namely "4 n".

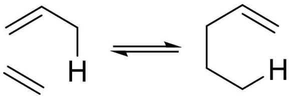
of a circle. The following is a hopefully nearly complete list of cases through ten electrons. Only reactions involving single and double bonds are enumerated. In all cases, a hydrogen atom (H) component may be replaced by and alkyl group (R)."[116]

The first and third pages of the "Catalogue" produced after the summer of 1966 are reproduced in Figure 11 and Figure 12.[116] The catalogue includes the basic carbon (generic) skeletons that would incorporate electrocyclizations, cycloadditions, sigmatropic reactions, group transfers and eliminations. (Electrocyclizations appear on the "the last entry on page 2, just before the page reproduced in Figure 12 (not illustrated herein).) Hoffmann acknowledged "the assistance of W. J. Hehre and J. B. Lisle", two undergraduates who worked with him at Cornell in this research during the summers of 1965 and 1966.[116,129]

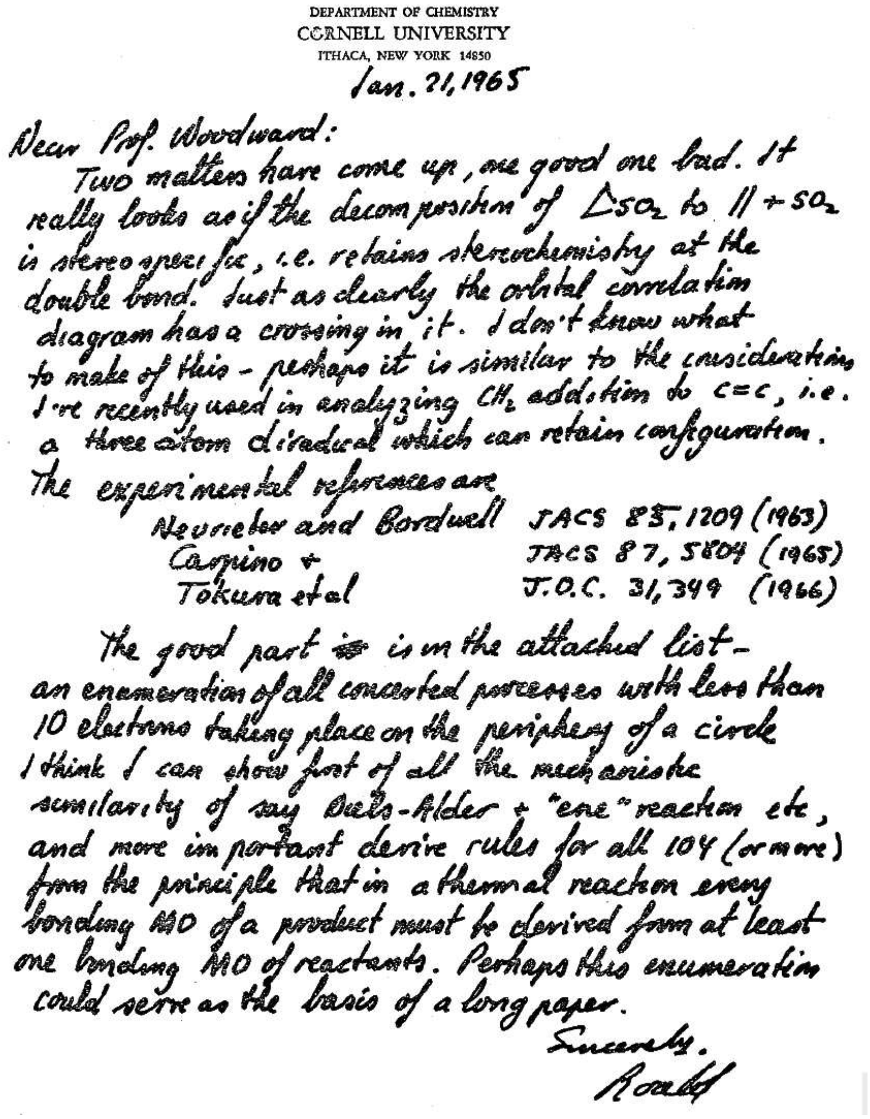
This was a far-reaching enumeration by Hoffmann, expanding the collection of reactions explicable by orbital symmetry control to an infinite set of possibilities. He anticipated that a catalogue of all pericyclic reactions would fit a simple structural scheme. In his March 5, 1966, letter to his friend and subsequent (1987) Nobel laureate Jean-Marie Lehn to which he attached the "Catalogue," Hoffmann wrote:

"Pushed by a desire to do something about unsymmetrical reactions which may be concerted, e. g., the 'ene' synthesis [Scheme 1], I've developed a way of analyzing any reaction, with or without symmetry. The attached, incomplete list shows some of the cases possible – there are about 110 reactions of cyclic topology involving ten or less electrons."[130]

The "Catalogue" was not truly what the title promised. Absent were some of organic chemistry's most important and historically-relevant *concerted* reactions, including classic concerted reactions whose mechanisms had been determined decades prior to Woodward and Hoffmann's publications.



Scheme 1. The ene reaction.



DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK 14850

Jan. 21, 1965

Dear Prof. Woodward:

Two matters have come up, one good one bad. It really looks as if the decomposition of $\triangle SO_2$ to $\parallel + SO_2$ is stereospecific, i.e. retains stereochemistry at the double bond. Just as clearly the orbital correlation diagram has a crossing in it. I don't know what to make of this - perhaps it is similar to the considerations I've recently used in analyzing CH_2 addition to $C=C$, i.e. a three atom diradical which can retain configuration. The experimental references are

Neureiter and Bordwell JACS 85, 1209 (1963)
Carpino + JACS 87, 5804 (1965)
Tokura et al J.O.C. 31, 349 (1966)

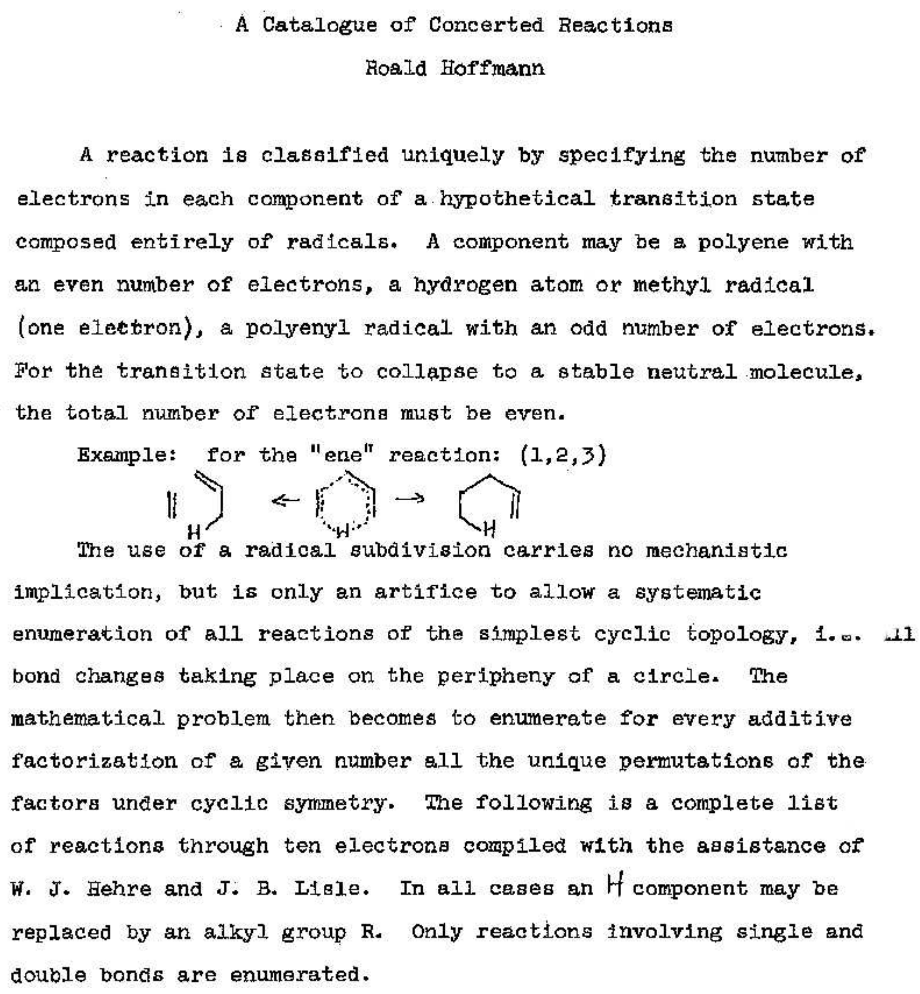
The good part is in the attached list - an enumeration of all concerted processes with less than 10 electrons taking place on the periphery of a circle. I think I can show first of all the mechanistic similarity of say Diels-Alder + "ene" reaction etc, and more important derive rules for all 104 (or more) from the principle that in a thermal reaction every bonding MO of a product must be derived from at least one bonding MO of reactants. Perhaps this enumeration could serve as the basis of a long paper.

Sincerely.
Roald

Figure 10. Cover letter from Hoffmann to Woodward in which Hoffmann attaches "an enumeration of all concerted processes with less than 10 electrons taking place on the periphery of a circle," i.e., pericyclic reactions. The letter is erroneously dated January 21, 1965.[128] Hoffmann surely meant January 21, 1966; see, for example, the citation to "Tokura et al … J.O.C. 31, 399 (1966)" could not have been recorded in 1965! Furthermore, Hoffmann arrived at Cornell in mid-June 1965. As this letter has several important statements from a historical perspective that are discussed in the text, unambiguous dating is a crucial historical datapoint.

Those mechanistic determinations are still and will always be considered core to organic chemistry. These include Ingold and Hughes's (non-pericyclic) S_N2 and E2 mechanisms and elaborations thereof, such as the Grob fragmentation[131] and the Eschenmoser fragmentation,[132] as well as nucleophilic and electrophilic aromatic substitution reactions (S_NAr and S_EAr).

There were several precedents to Hoffmann's "Catalogue." As his laboratory notebooks document, Hoffmann was a careful reader of the European and Russian chemical literature, not just American scientific literature. Nonetheless, he appears to have then forgotten that in 1957, Mathieu and Valls had complied a similar catalogue ("Le transfert électronique circulaire dans l'interprétation de certaines réactions de la Chimie organique" ("Circular electronic transfer in the interpretation of certain reactions of organic chemistry")[133]). I say "forgotten" in that Hoffmann cited the Mathieu and Valls publication on ca. February 22, 1965, on page 84 of his *Laboratory Notebook 16.* And in 1959, Yakov Kovovich Syrkin published a series of extensive articles on cyclic molecular rearrangements.[134–139] Hoffmann's catalogue is similar to a much more extensive collection of pericyclic reactions published by in 1967 by Alexandru T. Balaban's entitled



A Catalogue of Concerted Reactions

Roald Hoffmann

A reaction is classified uniquely by specifying the number of electrons in each component of a hypothetical transition state composed entirely of radicals. A component may be a polyene with an even number of electrons, a hydrogen atom or methyl radical (one electron), a polyenyl radical with an odd number of electrons. For the transition state to collapse to a stable neutral molecule, the total number of electrons must be even.

Example: for the "ene" reaction: (1,2,3)

The use of a radical subdivision carries no mechanistic implication, but is only an artifice to allow a systematic enumeration of all reactions of the simplest cyclic topology, i.e. all bond changes taking place on the peripheny of a circle. The mathematical problem then becomes to enumerate for every additive factorization of a given number all the unique permutations of the factors under cyclic symmetry. The following is a complete list of reactions through ten electrons compiled with the assistance of W. J. Hehre and J. B. Lisle. In all cases an H component may be replaced by an alkyl group R. Only reactions involving single and double bonds are enumerated.

Figure 11. Page 1 of Hoffmann's 18-page report entitled "A Catalogue of Concerted Reactions,"[116] Ithaca, NY, version produced after the summer of 1966. Note Hoffmann's acknowledgment of Warren J. Hehre and John B. Lisle, undergraduate students who worked with him during the summers of 1965 and 1966.

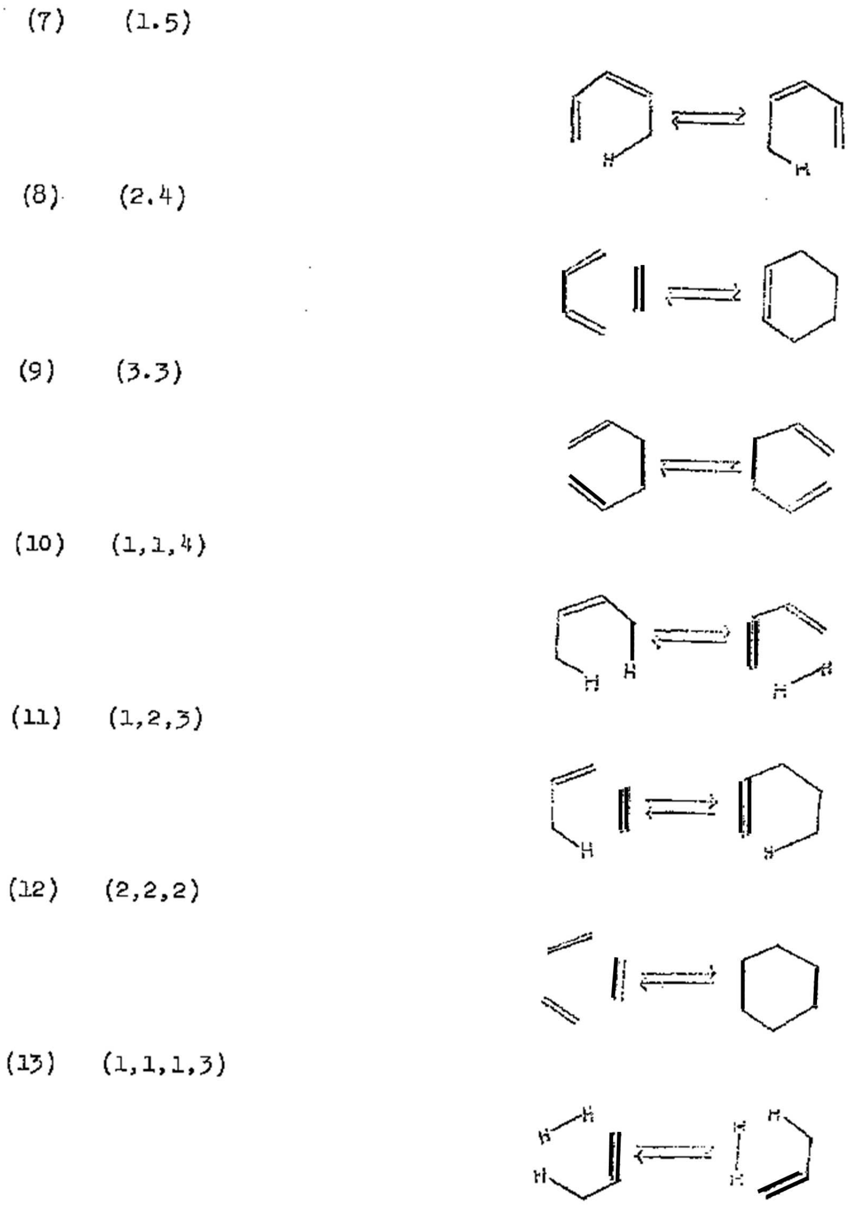
"Chemical graphs"[140] and by James B. Hendrickson[141] in 1975 entitled "The Variety of Thermal Pericyclic Reactions."[142] Regarding Syrkin, Hoffmann said,

> "Knowing how much theory Syrkin[143,144] (and his colleague M. E. Dyatkina[144,145]) knew, they were in a position to solve the electrocyclic and cycloaddition problems. I am impressed by the knowledge of the literature displayed in this paper. It was not easy to follow the world of chemistry literature in the USSR."[146]

Hoffmann's "Catalogue" was never published, even though Hoffmann included it in the first drafts of the 1969 *Angewandte Chemie* drafts, and it was retained in at least one of Woodward and Hoffmann's subsequent drafts. The publications by Balaban and Hendrickson, in particular, may well explain the fact that the "Catalogue" was never submitted for publication, Hoffmann being a salvager of research results, nonetheless. Hoffmann explained,

> "I offered the catalogue to Woodward. You can see its persistence in the series of Harvard drafts [of the *Angewandte Chemie* manuscripts]. In some sense, he was right to reject it. I do not want to escape any responsibility here; it could well have been a joint decision. Catalogues and enumerations are examples of no thinking; they are lists. Very mechanical, and orbital symmetry is not mechanical. Chemistry is not either. But sometimes, the making of lists, simple classification, is an early stage of understanding."[2,147]

One version of the *Catalogue* is reproduced in its entirety in the Supplementary Information.



(7) (1.5)

(8) (2.4)

(9) (3.3)

(10) (1,1,4)

(11) (1,2,3)

(12) (2,2,2)

(13) (1,1,1,3)

Figure 12. Page 3 of Hoffmann's 18-page report entitled "A Catalogue of Concerted Reactions,"[116] Ithaca, NY, after the summer of 1966. The first entry of "Six Electrons" on page 2 is 1,3-cyclohexadiene ⇋ 1,3,5-hexatriene, a prototypical electrocyclization. On page 3 are examples of cycloadditions, sigmatropic reactions, and group transfers and eliminations. Some of the bonds have been darkened by Seeman for improved visibility.

Who were the two undergraduates who worked with Hoffmann on the *Catalogue*? One was a Cornell undergraduate student, Warren J. Hehre. Hehre subsequently received his Ph.D. at Carnegie Mellon University with John A. Pople, later a Nobel laureate (1998). Hehre become a noted theoretical and computational chemist, first at the University of California at Irvine and subsequently as an entrepreneur in the application of quantum chemistry in chemical research.[148] In 1968, Hehre published an article[149] with Hoffmann and Hoffmann's first postdoctoral student, Akira Imamura, based in part on other research Hehre carried out as an undergraduate. The second undergraduate student was a 1966 summer intern named John B. Lisle. Lisle was a close friend of Hehre's in their youth in Pelham Manor, NY. Lisle was an MIT student who, like Hehre, later studied with Pople at

Carnegie Mellon. Unlike Hehre, Lisle did not complete a Ph.D. in chemistry, but focused his career in software engineering activities.[150] Lisle obtained the summer position at Cornell through the recommendation of Hehre. Some perforated continuous computer printer output relevant to the catalogue, with Lisle's name carefully recorded dated "07/21/66" exists today in Hoffmann's files. Hoffmann proudly showed me these pages in July 2024.

7. W-H 9: In "Aromaticity," Special Publication No. 21: "The Conservation of Orbital Symmetry"[104]

A. General Comments

On July 8, 1966, Woodward presented a lecture at the University of Sheffield, England at a symposium on *Aromaticity* initiated and hosted by William David Ollis. Ollis had been a postdoctoral fellow with Woodward and a member of the "total synthesis of strychnine"[151,152] team. Subsequently, Ollis jointed the Department of Chemistry at the University of Sheffield and ultimately became their professor of organic chemistry.[153]

Woodward's lecture was published as the culminating chapter in an 11-chapter monograph entitled *Aromaticity: An International Symposium Held at Sheffield, England, on 6th-8th July 1966* (Table 3).[154] Inspection of Table 3 reveals that the other authors were quite well-known chemists and mostly European. They all lectured and wrote on some aspect of aromaticity – other than Woodward. The symposium was held under the auspices of the Chemical Society (London) and served as the basis of a monograph published by this organization. (The Chemical Society joined with the Royal Institute of Chemistry, the Faraday Society, and the Society for Analytical Chemistry in 1980 to become The Royal Society of Chemistry.) H. C. Longuet-Higgins's chapter was rather brief, though perhaps no unexpected in that he was just then exiting chemistry to enter into the field of musicology and an early stage of artificial intelligence. Notables are those individuals not involved in the symposium and monograph though they were arguably among the leaders in aromaticity research at the time: Doering, Ronald Breslow, Thomas Katz, and Edgar Heilbronner.

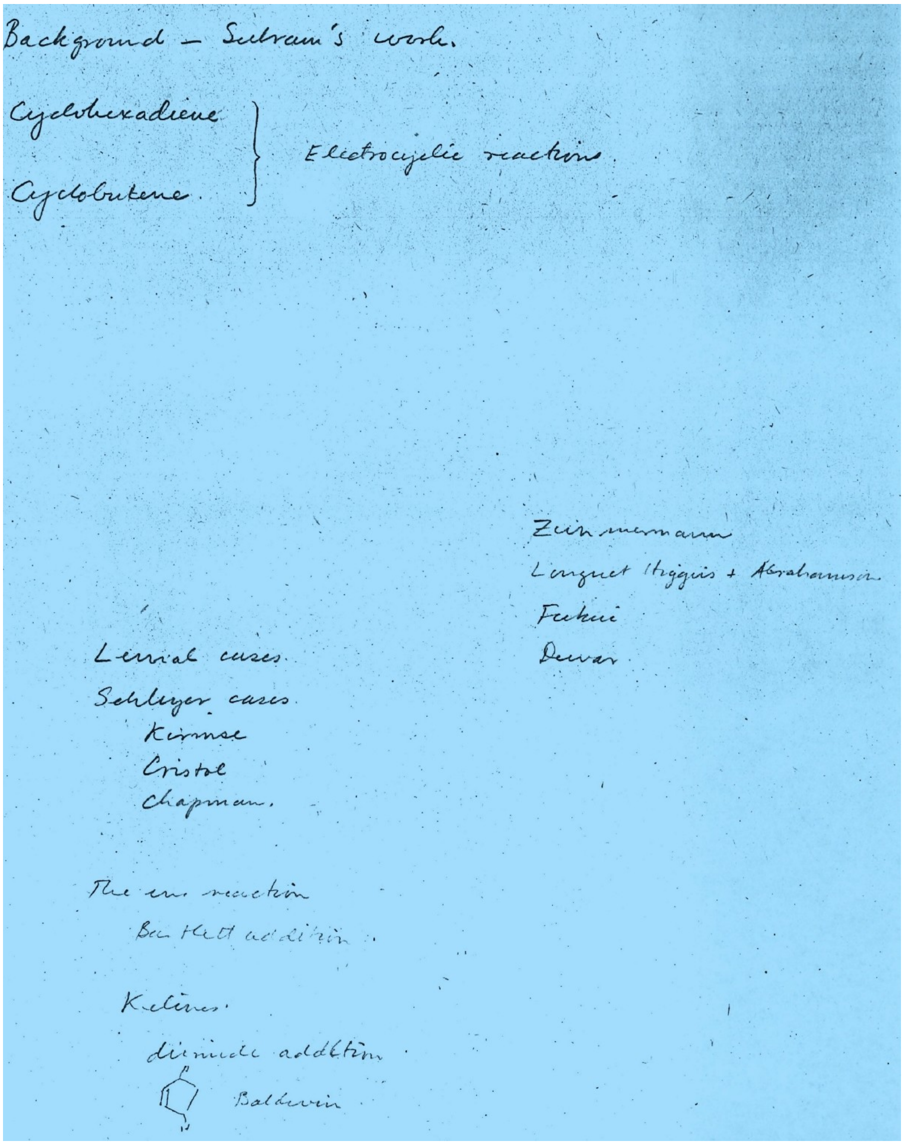
Woodward began the development of his lecture and essay is a manner not atypical of him: he drafted an outline (Figure 13). While this page was found within Woodward's papers in one of the many folders dealing with pericyclic reactions, the identification as to which of the various W–H publications it belongs to is based on an overlap between the topics listed in Figure 13 and Woodward's publication[104] (W–H 9) based on his lecture. Ironically, several of the names on the outline were ultimately not included in the text. Woodward could have discussed – even should have discussed and cited – Howard E. Zimmerman's[155–157] and Michael J. S. Dewar's[158–160] use of aromaticity and antiaromaticity for pericyclic reactions. Woodward did not. This omission is discussed further in Section 6e.

Woodward's chapter begins with a short preface:

> [The above] *This* is essentially a direct transcript of the lecture I presented in Sheffield on 8 July 1966, amended only by deletion of egregious errors and a small amount of relatively

Table 3. Chapters in *Aromaticity: An International Symposium Held at Sheffield, England, on 6th-8th July 1966 (Special Publication No. 21)* published in 1967 by the Chemical Society (London)[154]

Authors	Chapter title	Page
Anonymous	Table of Contents	*v*
W. David Ollis	"Introduction"	1
Saul Winstein	"Non-classical Ions and Homoaromaticity"	5
Sir Robert Robinson	"The Concept of the Aromatic Sextet"	47
Rolf Huisgen	"Cycloaddition Reactions of Mesoionic Aromatic Compounds"	51
Franz Sondheimer, J. C. Calder, J. A. Elix, Y. Gagni, P. J. Garratt, K. Grohmann, O. Di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky	"The Annulenes and Related Compounds"	75
H. Christopher Longuet-Higgins	"Paramagnetic Ring Currents in the [4 *n*]-Annulenes"	109
Emanuel Vogel	"Aromatic 10 π-Electron Systems"	113
John H. Ridd	"Electrophilic Substitution in Deactivated Aromatic Systems"	149
Michael P. Cava	"Some Recent Aspects of the Chemistry of Condensed Cyclobutane Aromatic Compounds"	163
Michael J. S. Dewar	"Some Recent Developments in the Theory of Conjugated Systems"	177
R. B. Woodward	"The Conservation of Orbital Symmetry"	217



Background – Subram's work.

Cyclohexadiene }
Cyclobutene. } Electrocyclic reactions.

Zimmermann
Longuet Higgins + Abrahamson.
Fukui
Dewar.

Lemal cases.
Schleyer cases.
  Kirmse
  Cristol
  Chapman.

The ene reaction
  Bartlett addition.

Ketenes.
  diimide addition.
  Baldwin.

Figure 13. Woodward's partial outline of his Aromaticity lecture and essay.[161]

unimportant and incompletely developed factual material, by modification of phrases of action ancillary to the live explication of visual material, and [by removal of trivial material, and] by removal of the more obvious gaucheries which so often differentiate the spontaneously spoken from the thoughtfully written language. Those who have had the devastating experience of seeing such ~~they may have been sanguine such transcript~~ transcripts of what they may well have imagined to be ~~and eloquent a lecture clearly presented of lucid and elegant expositions~~ their lucid, well-phrased, or even eloquent expositions, will appreciate the reluctance with which I have allowed this material ~~to appear in print to be published~~ to be laid bare here. Only the most ~~advocacy by the S~~ powerful advocacy by Professor Ollis of the view that a mean fraction of a loaf is better than none has brought me to perpetrate this literary offense. R.B.W."[104] [Text within brackets was in the original handwritten draft but not in the final publication] [Text *italicized* was not in the original draft but is unitalicized in the final version.] [Text crossed through was ~~crossed through~~ in the original handwritten draft but not in the published version.]

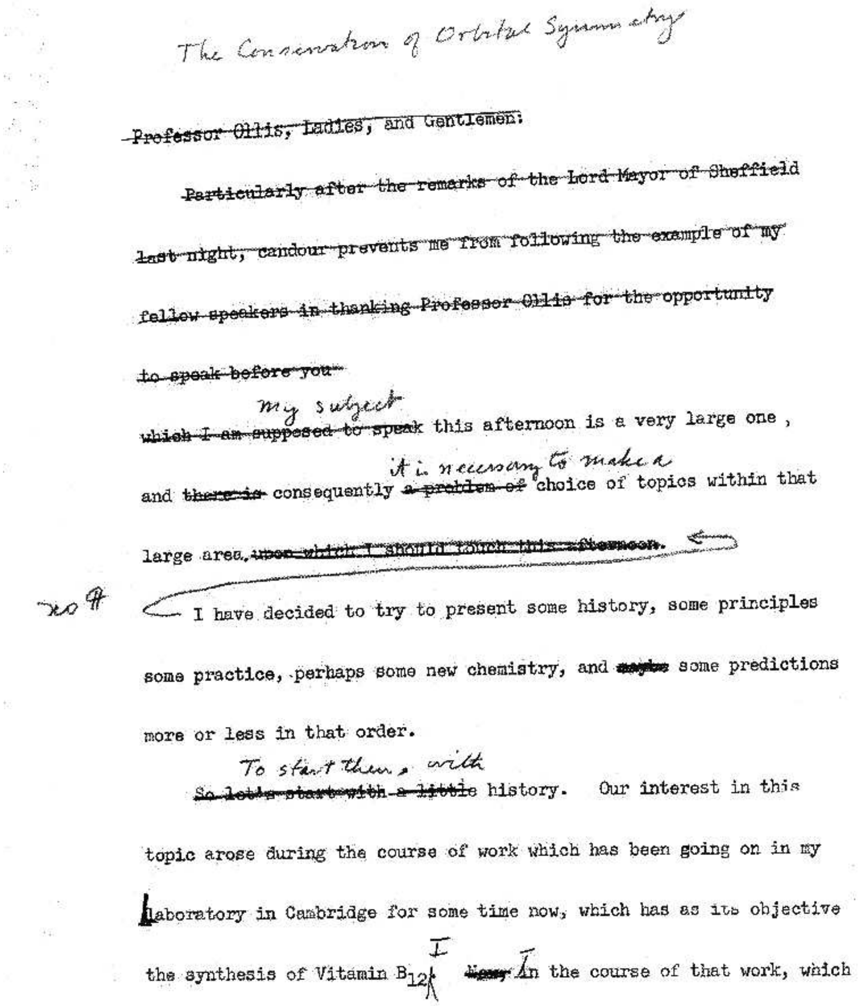
I can well imagine that Woodward overstated his reluctance to publish this essay. Here, Woodward was handed the opportunity to record in an authoritative fashion absent any peer review his perspective of the history of the first five

Woodward-Hoffmann *JACS* communications – because that was all that he and Hoffmann had published together by that time. It was a perfect opportunity and an open, uncensored microphone.

The essay is an important publication for many reasons. Perhaps most importantly, Woodward told the history of the origination of the Woodward-Hoffmann rules, and he is the sole author of this particular telling. Hoffmann was not a co-author – though he is acknowledged in the last paragraph – and as discussed later, Hoffmann was not provided a preprint for his review. Specifically, Hoffmann does not even recall seeing this publication until long after it was published.[86] Woodward's *Aromaticity* publication is also important because it is the first public pronouncement of the term "conservation of orbital symmetry."

It could be argued[2] that, before the fact, Woodward had no intention of publishing his lecture. But W. David Ollis was certainly eager to have a chapter from Woodward, so he might well have presented Woodward with a transcript of his lecture, thereby rendering the task of writing a publication somewhat mute. I believe otherwise. Within the Woodward Archives at Harvard is a complete lecture in Woodward's handwriting, the first page of which is reproduced in Figure 14. Woodward was being very thorough and detailed in his draft, as indicated by the original text of his introduction:

"Particularly after the remarks of the Lord Mayor of Sheffield last night, candor prevents me from following the example of my fellow speakers in thanking Professor Ollis for the opportunity to speak before you … "[104]



The Conservation of Orbital Symmetry

~~Professor Ollis, Ladies, and Gentlemen:~~

~~Particularly after the remarks of the Lord Mayor of Sheffield~~
~~last night, candour prevents me from following the example of my~~
~~fellow speakers in thanking Professor Ollis for the opportunity~~
~~to speak before you~~

my subject
~~which I am supposed to speak~~ this afternoon is a very large one ,

it is necessary to make a
and ~~there is~~ consequently ~~a problem of~~ choice of topics within that
large area. ~~upon which I should touch this afternoon.~~

no ¶ I have decided to try to present some history, some principles
some practice, perhaps some new chemistry, and ~~maybe~~ some predictions
more or less in that order.

To start then, with
~~So let's start with a little~~ history. Our interest in this
topic arose during the course of work which has been going on in my
laboratory in Cambridge for some time now, which has as its objective
the synthesis of Vitamin B_{12}. ~~Now~~ In the course of that work, which

Figure 14. First page of Woodward's typewritten lecture given on July 8, 1967. It is addressed to "Professor [William David] Ollis, Ladies, and Gentlemen" and begins, "Particularly after the remarks of the Lord Mayor of Sheffield … " Woodward then used the lecture to derive a first draft of what would become his chapter in the *Aromaticity* monograph.[104] At the very top is the first documented use of the term "The Conservation of Orbital Symmetry."

Woodward was prepared to acknowledge the Lord Mayor who addressed the current audience the night before Woodward's lecture. That text is crossed out, presumably because it was unnecessary and irrelevant for use in the printed version of Woodward's lecture. Thus, I surmise that Woodward had carefully prepared his lecture, then used that text with upgrades for his chapter[104] in the monograph.[162] Several other pages of Woodward's handwritten manuscript have been reprinted in Peter J. T. Morris and O. Theodor Benfey's monograph on Woodward.[163]

There are several factors that give the essay additional imprimaturs of authenticity, orthodoxy, and legitimacy:

- Woodward's *Aromaticity* essay was published a year after the lecture and two years after the publication of Woodward and Hoffmann's five *JACS* communications. This timing provided the theories and historical stories described therein a sense of chronological veracity and also some real degree of expansivity (due to the many succeeding experimental publications with new examples and tests of the generalized selection rules) and ripening.
- The community was receptive to an update from Woodward and Hoffmann, and if not from both, then from Woodward, along with their synthesis of the concepts.
- The organic chemistry community had jumped immediately onto the test-predict bandwagon for the Woodward-Hoffmann rules, and Woodward reported on these developments in his essay (W–H 9). He had an adoring audience, based also in part on the fact that he was Woodward, the Pope of Organic Chemistry.[66,68]

Woodward's chapter consists of three parts, and I shall comment on each of these in sequence. I shall also include a fourth section that discusses Woodward's handling of credit.

b. The Historical and Autobiographical Section

The first nine pages of the *Aromaticity* essay focus exclusively on Woodward's historical entry into the Woodward-Hoffmann rules. Key to Woodward's story is his four – actually five – mysterious reactions. During the 1950s and early 1960s, Woodward kept track of reactions whose mechanisms were unknown to him and that unknowing for Woodward was a source of great discomfort. In his 1973 Cope Award address, Woodward recalled that,

"whenever I was tempted to become too complacent, there arose in my mind the spectre of these four mysterious reactions."[164,165]

In this 1968 *Aromaticity* publication, Woodward presented a fifth mysterious reaction, one that arose in late 1963 or early 1964 during his last unsuccessful approach to the total synthesis of vitamin B_{12} and before the beginning of his ultimately successful collaboration with Albert Eschenmoser. The key steps in Woodward's proposed synthesis that led to this fifth mysterious reaction were performed by his postdoctoral student Subramania Ranganathan.

A summary of Ranganathan's reactions is shown in Figure 15. This key step in Woodward's vitamin B_{12} synthetic plan was the thermal cyclization of the 1,3,5-triene **1** to yield **4**. However, Mother Nature and organic chemistry did not follow Woodward's plan. Rather than **1** → **4**, thermal ring closure of **1** led to the 1,3-cyclohexadiene **3** instead.[166,167] This synthetic calamity ultimately had two spectacularly successful though unintended consequences. First, Woodward changed his synthetic strategy and simultaneously began his collaboration with Albert Eschenmoser. Ultimately vitamin B_{12} was synthesized, actually by several routes.[36,37,42,44] Second, the chemistry shown in Figure 15 led in due course to Woodward's collaboration with Hoffmann and the discovery of the principle of conservation of orbital symmetry. Ranganathan's chemistry, essentially Figure 15, and its connection to the Woodward-Hoffmann rules were told for the first and only time by Woodward in his Sheffield lecture and *Aromaticity* chapter (W–H 9).[104]

c. The Theoretical Section

The next eight pages of his *Aromaticity* essay[104] summarized Woodward's exposition of the quantum chemical theories underlying the mechanism of electrocyclizations, cycloadditions, and sigmatropic reactions. These discussions were brief and of mixed pedagogical value, understandable for electrocyclizations, less so for cycloadditions, and confusing at best and misleading at worst for sigmatropic reactions. This descending educational quality is completely consistent with Woodward and Hoffmann's performance in their first three *JACS* communication on these topics, as well as in their later review articles and substantive treatise (and consistent with textbook expositions by other authors as well). The theoretical underpinning of the mechanism of sigmatropic reactions has not been presented well since its first report in 1965[5] though recent attempts have been made.[16,171] Details of Hoffmann's research that led to the third W–H communication on sigmatropic reactions, as well as a carefully constructed and organized tutorial on the simple MO theories used by Hoffmann in the spring of 1965, are presented in a previous publication in this series.[16]

It is worthwhile to point out the special words Woodward used to transition from Ranganathan's vitamin B_{12} chemistry shown in Figure 15 to the generalizations of electrocyclic reactions, the easiest of the types of pericyclic reactions to

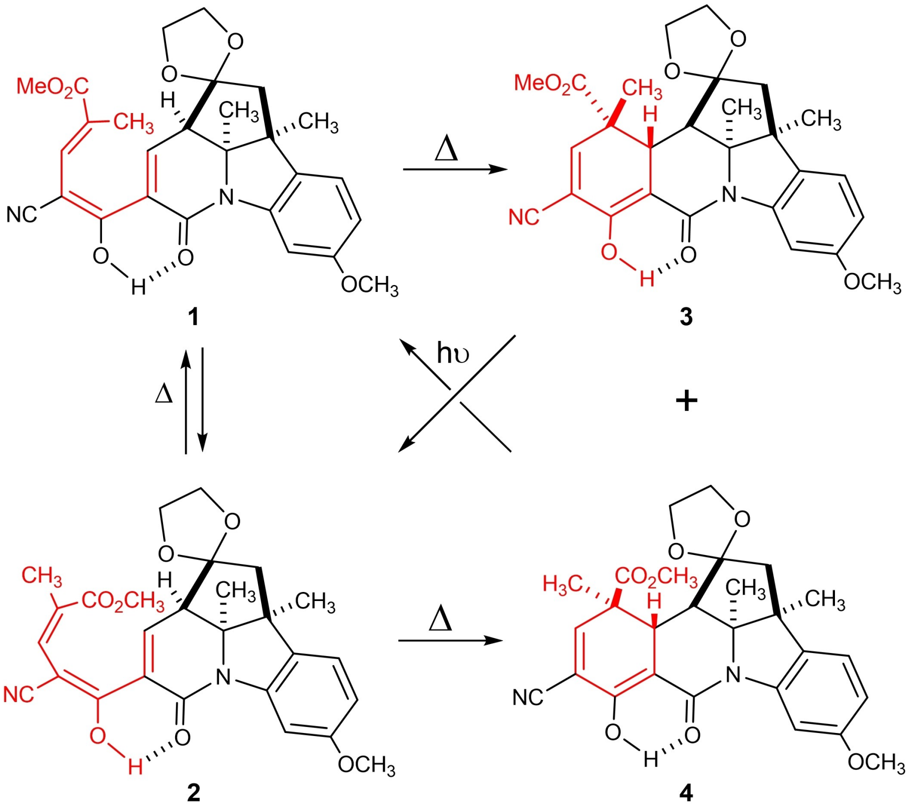
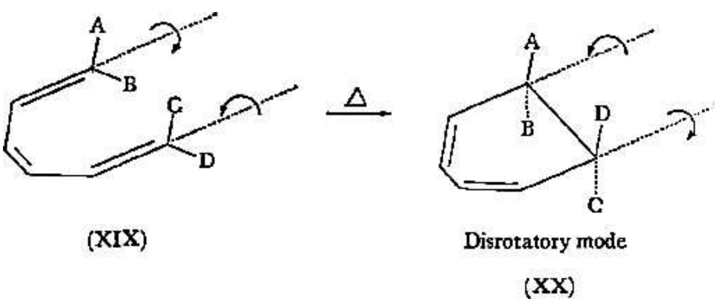


Figure 15. Graphical reproduction from Woodward's autobiographical discussion of the origins of the Woodward-Hoffmann rules published by Woodward in 1967.[104,167] Woodward described Subramania Ranganathan's 1963 – early 1964 set of reactions[166] that were central to Woodward's ultimately unsuccessful route to the total synthesis of vitamin B_{12}. The several sets of stereospecific reactions in this figure became Woodward's fifth mysterious reaction that ultimately led to his collaboration with Hoffmann in May 1964 (and his collaboration with Eschenmoser in 1965 on the synthesis of vitamin B_{12}). Woodward's proposed synthetic path to vitamin B_{12} included the transformation of **1** into **4** via an electrocyclization but **3** was formed instead. Woodward's inclusion of this scheme in his *Aromaticity* chapter (W–H 9) was his first and only publication of Ranganathan's chemistry by Woodward, though it has been discussed and reprinted several times thereafter by others[44,167–170] (typically without the "plus sign" between **3** and **4**).

explain using MO concepts. Woodward wrote in his *Aromaticity* chapter,

"Now let us strip the discussion of the impedimenta attendant upon our original preoccupation with vitamin B_{12} synthesis [i. e., the structures in Figure 15], and reduce the problem to its essentials. What we were dealing with was a triene cyclization … " [**XIX** → **XX**; Scheme 2] [This quote is an exquisite example of the beauty of Woodward's words, a topic that I have documented in full detail.[79,172–176]]



Scheme 2. A graphical excerpt from Woodward's *Aromaticity* publication[104] illustrating the disrotatory electrocyclization shown in Figure 15. An early beautiful illustration of the role of conformation in these reactions, i. e., the 1,3-cyclohexadiene **XX** is not planar as drawn, was provided by Baldwin and Krueger in 1969.[177]

In his *Aromaticity* essay, Woodward then presented a simplified HOMO (highest occupied molecular orbital) overlap interaction analysis of electrocyclizations, cycloadditions, and sigmatropic reactions. Let us look at his theoretical explanations in detail.

First, for electrocyclizations, Woodward considered the HOMOs of 1,3,5-hexatriene (**XXIV**; Scheme 3). The phases of the terminal carbons C(1) and C(6) of the HOMO of **XIX** are the same; thus, a disrotatory motion shown in **XXIV** would result in bonding between C(1) and C(6). Alternatively, a disrotatory motion of the σ-bond C(5)-C(6) MO of 1,3-cyclohexadiene **XX** shown in **XXV** would correlate with the phases of C(1) and C(6) of the ring-opened 1,3,5-hexatriene (**XXVI**). In this publication (W–H 9), Woodward also drew the correlation diagram for the electrocyclization **XXIV** $\leftrightharpoons$ **XXV** (not reproduced herein), following the precedent of H. Christopher Longuet-Higgins and Edward W. Abrahamson.[178] This quantum chemical explanation of electrocyclizations is theoretically equivalent to the HOMO overlap interaction method that was published in the first Woodward-Hoffmann 1965 communication.[3]

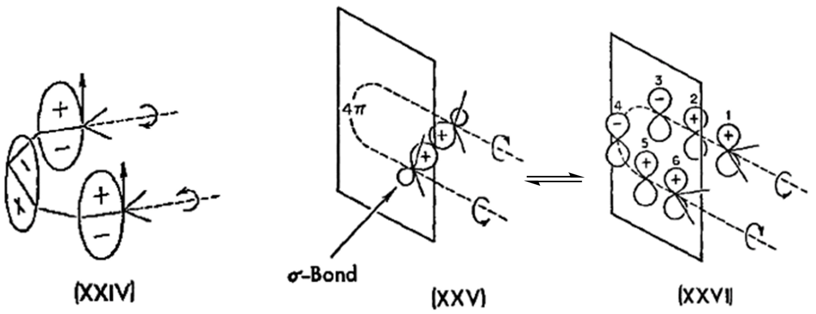
Second, for cycloadditions, Woodward continued his story as follows:

> "Now, viewing the system in this way led us to realize very soon that similar considerations should be applicable to a wider variety of chemical phenomena. What we are saying in the analysis of the problem just presented is that the conversion of cyclohexadiene into hexatriene is an addition reaction, in which the two components are a diene on the one hand and the single bond which is being broken on the other. From here it is of course the very shortest step to realize that precisely similar considerations are applicable to cycloaddition reactions."[104]

In point of fact, Woodward's description, i. e., "led us to realize very soon … the very shortest step",[104] of the expansion of the W–H rules from electrocyclizations to cycloadditions and then to sigmatropic reactions was and is *not* in accord with the historical facts. Woodward and Hoffmann's route from electrocyclizations to cycloadditions to sigmatropic reactions was laborious and not at all stepwise nor continuous nor linear. Chronologically, Hoffmann's research was short in terms of months. In terms of conceptual advances, Hoffmann advanced in short steps that were nonlinear, often discontinuous, and often backwards, laced with confusion and uncertainty. (Perhaps it felt as if it were "the shortest step" to Woodward because it was not he who was doing the research and perhaps Hoffmann had not shared with Woodward his trials and tribulations.)

After Woodward and Hoffmann's submission of their first communication on electrocyclizations, neither of them had any anticipation of future collaborative research. None.[15] When Hoffmann discovered the mechanism of cycloadditions,[4,15] neither he nor Woodward had any anticipation of either the sigmatropic problem nor that its solution would involve orbital symmetry.[5,16] And the analysis of the stereochemistry of the Diels-Alder reaction[6] and Cope reaction[7] – neither of which was anticipated by Woodward or Hoffmann – required the novel use of secondary orbital interactions to distinguish between several W–H allowed reactions.

Back to Woodward's *Aromaticity* essay. Woodward used a previously unpublished method to analyze pericyclic reactions, that being a frontier molecular orbital (FMO) deconstruction approach (Figure 16B). He applied this method for two similar analyses, one for the W–H thermally forbidden [2+2] cycloreversion of cyclobutene to two ethenes, and one for the retro-Diels-Alder reaction of 1,3-cyclohexadiene to 1,3-butadiene and ethene (Figure 16). Let us follow his ideas for the latter transformation. Though unstated explicitly by Woodward in his text, the symmetry element he appropriately used was the plane of symmetry shown in Figure 16A. Woodward explained his analysis as follows:



Scheme 3. A graphical excerpt from Woodward's *Aromaticity* publication[104] illustrating a disrotatory electrocyclization with the HOMOs shown. Each oval in **XXIV** is a shorthand representation of two adjacent atomic orbitals having the same phase. This shorthand can be confusing, and while used by others than Woodward in the mid-1960s, it is not recommended and rarely, if ever, used today.

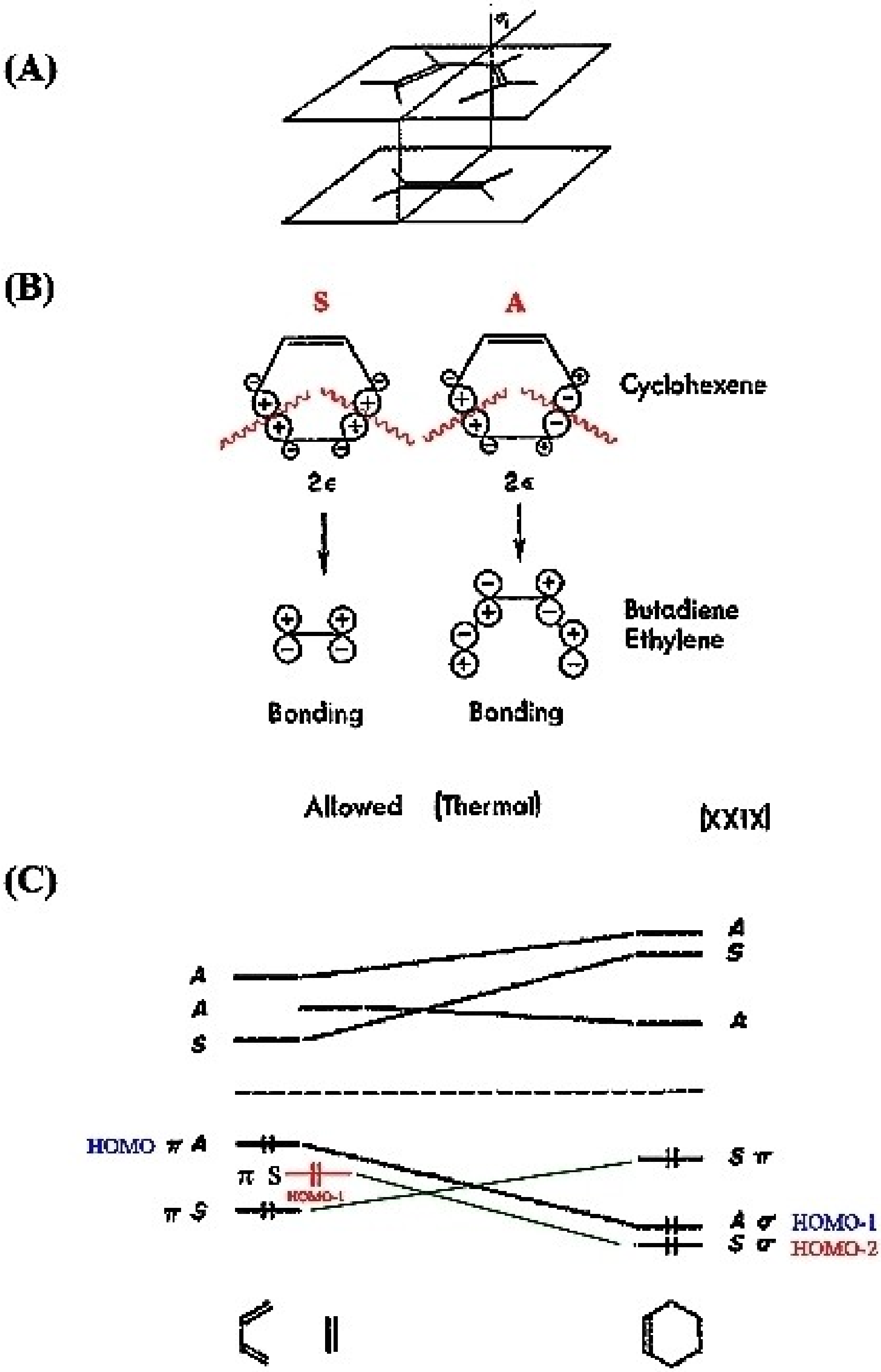


Figure 16. (A) Symmetry element used here is the plane of symmetry shown.. (B) In this graphic taken from Woodward's *Aromaticity* chapter,[104] Woodward cleaved the σ-bonds as shown by the red squiggly lines to form the HOMO of ethylene and the HOMO of 1,3-butadiene. This is essentially a correlation diagram, absent the other key MOs, symmetry elements, and relative energies of the MOs, analogous to that produced by Zimmerman and Zweig in 1961 for a sigmatropic reaction.[179] (C) The correlation diagram that plots the MOs of the reactants with the MOs the products, as specified in (B). The green correlation lines for the four symmetric (S) molecular orbitals differ from those in Hoffmann and Woodward's 1965 *JACS* publication on cycloadditions (see Figure 17). The MOs identified in red and blue font correlate (B) and (C). The non-crossing rule[180–182] for MOs having the same symmetry would result in a correlation diagram in which the green lines in (C) match the correlation diagram MO levels in Figure 17B. Note: All the text and lines in color in this figure were added by Seeman. The chemical pictograph in (A) and the correlation diagram in (C) are reproduced in the former and adapted in the latter with permission from R. Hoffmann, R. B. Woodward, *J. Am. Chem. Soc.* **1965**, *87*, 2046-2048. Copyright 1965 American Chemical Society.

"When we consider the cleavage of the two σ-bonds [in Figure 16B], we see that two of the electrons (those from the fully symmetric molecular orbital [on the left]) can pass into the bonding, symmetric orbital of the ground-state ethylene molecule. But what about the other two? In this case they pass into the asymmetric highest filled bonding level of the butadiene molecule. That is to say that, in this case, *all four of the electrons can pass into bonding levels of the two products*, namely ethylene and butadiene, with *conservation of orbital symmetry.* This, then, is a *symmetry-allowed* process."[104] [italics in the original]

Let us compare Woodward's argument in Figure 16 (the *Aromaticity* publication (W–H 9[104] published in 1968) with what Woodward and Hoffmann published for the same reaction in their second 1965 *JACS* communication on cycloadditions reproduced in Figure 17.[4] A visual comparison of Woodward's correlation diagram (Figure 16B) with Woodward and Hoffmann's correlation diagram (Figure 17B) reveals several inconsistencies. In a nutshell, the two MOs with S symmetry in the ethylene – 1,3-butadiene complex correlate with different MOs in Figure 16B as compared to Figure 17B.

What is causing this inconsistency between Woodward's publication in *Aromaticity* (W–H 9) and W–H's second *JACS* communication in 1965 (W–H 2)? Is it simply the arbitrary placement of the MO energies of the two symmetric MO levels relative to each other? The [4+2] cycloaddition is going to be W–H allowed whether the correlation diagram looks like Figure 16 or Figure 17. As Woodward wrote in W–H 9, "all four of the electrons can pass into bonding levels of the two products." Furthermore, Figure 16 converts to Figure 17 when applying the MO no-crossing rule,[51,180,181,183–185] i. e., potential energy curves (including MO energy levels) corresponding to electronic states of the same symmetry type cannot cross.

There are several reasons I have pointed out this inconsistency between Woodward's theoretical justification for [4+2] allowedness in W–H 9[104] and Woodward and Hoffmann's theoretical justification in W–H 2.[4] First, either Woodward himself did not see this distinction, or he considered it to be unimportant. Otherwise, he could have illustrated his *Aromaticity* essay[104] with the same correlation diagram that appeared in Woodward and Hoffmann's second *JACS* publication[4] (Figure 17B)! I speculate that Woodward did not refer back to his earlier publication when he drafted the *Aromaticity* lecture. Hoffmann agrees with this analysis.[2]

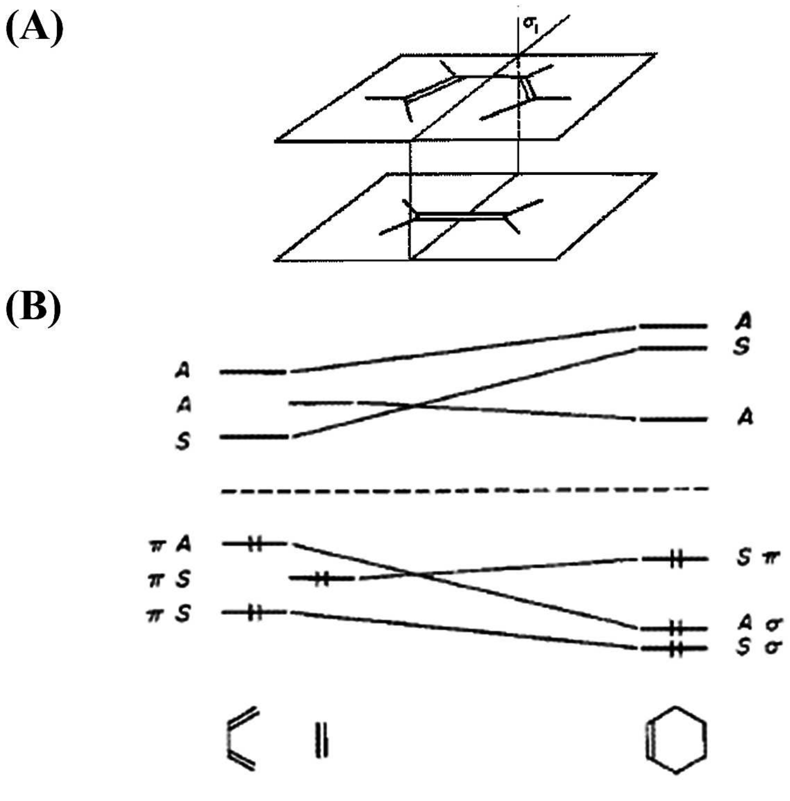


Figure 17. (A) Symmetry element used for [4+2] cycloadditions. (B) Correlation diagram for the [4+2] Diels-Alder cycloaddition taken from Woodward and Hoffmann's second 1965 *JACS* communication.[4] Reprinted with permission from R. Hoffmann, R. B. Woodward, *J. Am. Chem. Soc.* 1965, *87*, 2046–2048. Copyright 1965 American Chemical Society. This is also the correlation diagram that appears as Figure 11 in their 1969 treatise (W–H 11).[12,13]

Second, it seems that Woodward wanted to explain several types of pericyclic reactions using the same MO tool. Third, as mentioned above, Figure 16C transforms into Figure 17B when considering the no-crossing rule.

Would the discrepancy between the correlation diagrams (Figure 16C and Figure 17B) have been seen by Hoffmann, had Woodward shown him a draft of the Sheffield lecture? We do not know for certain; as I've said, there is no evidence that Hoffmann saw the Woodward text in any form, before or after its delivery.[86]

As for sigmatropic reactions, Woodward's application of the molecular orbital deconstruction explanation was faulty, incomplete, and based on circular logic. But I quickly add several thoughts. First, Woodward could have used the HOMO overlap interaction method that he and Hoffmann provided in their third *JACS* communication of 1965,[5] even though that had its own weaknesses. But Woodward chose otherwise, probably for consistency. Perhaps he wanted to use a single MO tool for electrocyclizations, cycloadditions, and sigmatropic reactions. I shall not discuss this matter further. Interested readers can delve more deeply into Woodward's treatment of sigmatropic reactions themselves.[104]

D. New Personal Histories and New Experimental Observations

In the third and last section of the *Aromaticity* essay (16 pages), Woodward gently and proudly presented an extensive series of stereospecific and regiospecific pericyclic reactions whose mechanisms were explicable only with orbital symmetry control, as illustrated in Figure 18. Woodward, of course, assumed that all these were concerted reactions. The previous W–H publications, being communications, were brief and contained limited examples.

In W–H 9, Woodward included a wide range of examples, as illustrated in Figure 18. Several of these include stereospecificity, a keynote in the mechanism of pericyclic reactions. Example D in Figure 18 is, of course, not a stereospecific reaction.

Woodward was now really in his realm, the universe of transformations in organic chemistry. In my characterization, Woodward presented 12 different types of reactions explicable by the W–H selection rules the way a curator would walk visitors slowly and deliberately through the galleries of an art museum. As a curator, Woodward was quietly pleased with the achievements of others as he explained the stereochemistry of the reactions and their mechanisms citing orbital symmetry control. Woodward's was a soft sell; there was no attempt to overpower the reader. Rather, his presentation was like an warm welcome to the home of a contented wise guru.

So, what was new in Woodward's lecture and text?

- Woodward's personal history and his antecedents to the W–H story.
- The Ranganathan chemistry (Figure 15).
- Woodward's knowledge and use of MO theory. In the previous W–H joint publications, Hoffmann wrote the text dealing with MO theory. In W–H 9, Woodward wrote the MO-based explications.
- Woodward also firmly declared his role in the Woodward-Hoffmann story. This was a role that would later be challenged by E. J. Corey in 2004[187,188] and defended by Hoffmann shortly thereafter[189] and still today.[86]
- We also see Woodward's pride in the W–H rules, in their power and sweep. Of all the topics that Woodward could have chosen for his *Aromaticity* lecture and publication, from his numerous research programs at Harvard and at the newly-created Woodward Research Institute in Basel,[190,191] he chose the conservation of orbital symmetry. It also fit Ollis's aromaticity theory best from Woodward's current research programs – though ironically, Woodward did not cite the Zimmerman's and Dewar's aromatic transition state explanation.[155,156,158,159] All this is telling.

E. Woodward Giving Credit

There is a dark side to Woodward's essay. It was Woodward's way of providing credit in this single-author W–H publication.

First, I will speak of Woodward's credit to Hoffmann. The first sentence in the essay's final paragraph reads:

> "I should like now to acknowledge my warm appreciation of the most pleasant, stimulating, and fruitful collaboration of Roald Hoffmann, who has been my partner in developing the principles of orbital symmetry conservation, and their applications."[104]

I have previously commented that Hoffmann did not include Woodward as a co-author in Hoffmann's 1966 publication in the *Transactions of the New York Academy of*

Hoffmann feels certain that he had not seen Woodward's advanced draft. Otherwise, he would have urged Woodward to provide a somewhat modified theoretical discussion.[186] The extensive MO reasoning that Woodward's manuscript (W–H 9) contains suggests that he felt that he had mastered qualitative MO perturbation theory quite sufficiently and satisfactorily. For him, there was no need to consult with Hoffmann.

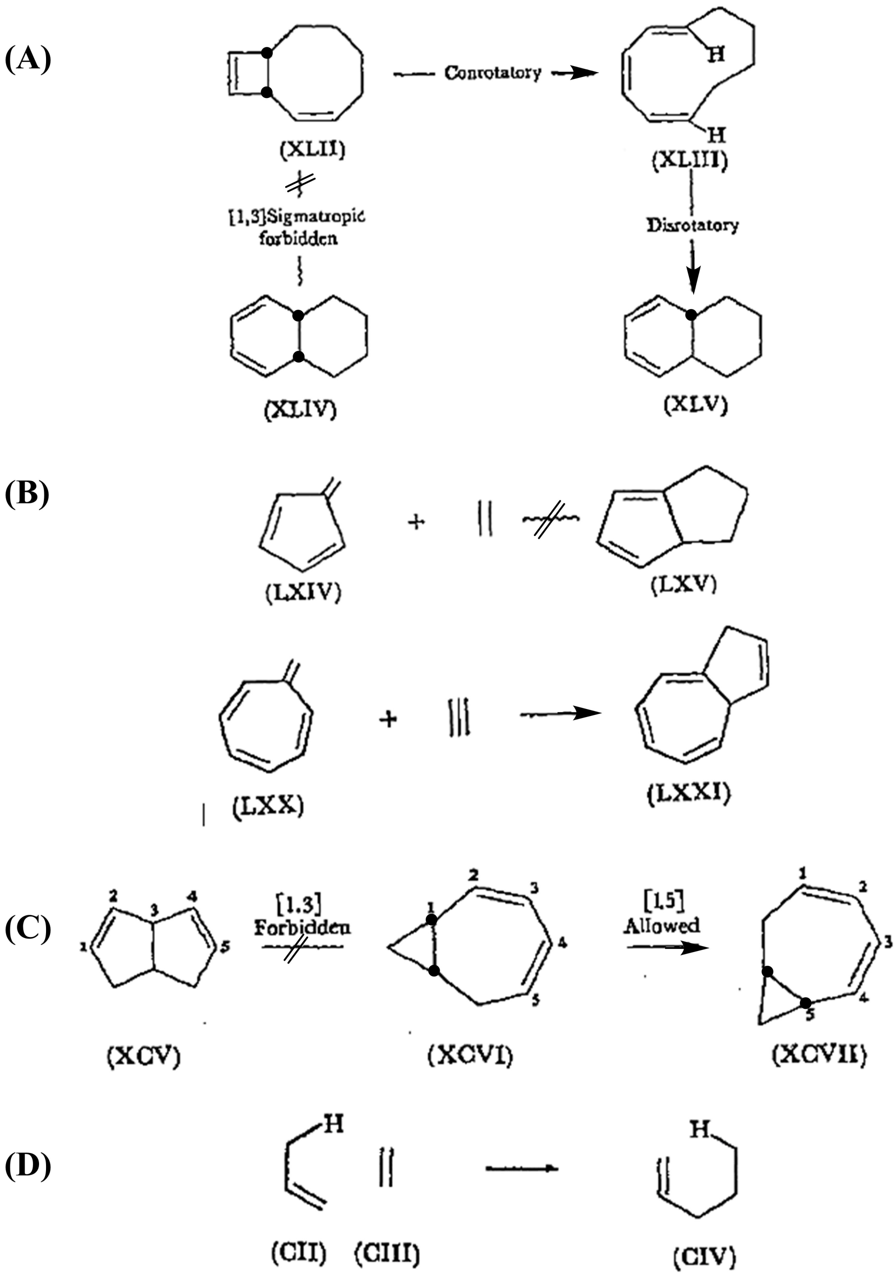


Figure 18. Examples from Woodward's *Aromaticity* publication of alternations in pericyclic reactions within the W–H allowed and forbidden schema: (A) electrocyclizations; (B) cycloadditions; (C) sigmatropic reactions; and (D) the ene reaction. These graphics illustrate the range of chemistry governed by the principle of conservation of orbital symmetry, as Woodward envisioned it in 1967.[104] Note that all of these reactions involved hydrocarbons though Woodward included a number of reactions with hetero-substituted compounds. Adapted from: R. B. Woodward, "The Conservation of Orbital Symmetry" in *Aromaticity: An International Symposium Held at Sheffield on 6th-8th July 1966*, Special Publication No. 21, pp. 217–249, The Chemical Society (London), London, 1967.

Sciences (see Section 4) though he did credit Woodward in the first sentence of the second paragraph of that publication:

"In collaboration with R. B. Woodward at Harvard, we have used a similar approach for the study of concerted reactions."[51]

Should Hoffmann have been a co-author in Woodward's publication in *Aromaticity*? If one goes solely or largely by the standard practices of the day, the answer is, "No." Furthermore, Woodward is correct, that Hoffmann was his "partner." But again, an excellent case could be made that Hoffmann's contributions were so great that there could not have been any

W–H publications on cycloadditions, sigmatropic reactions, cheletropic reactions, and group transfers if it had not been for Hoffmann. As was well accepted in the 1960s, there are many valid and less-than-valid justifications – or rationalizations – that were made by the principal investigators regarding authorship before there were formal publication codes regarding authorship as there are today.[192–194]

As Hoffmann recounted:

"I think it's the transcript of a lecture that he was prevailed upon to publish – not that he didn't choose carefully what to publish. I think he was telling in that paper the history as it related to the B_{12} synthesis origins. And I had no stake in that. I have never felt bad about being left out as a coauthor on this one. Or any paper Woodward wrote."[85]

Second, I speak of Woodward's credit to H. Christopher Longuet-Higgins, then the professor of theoretical chemistry at the University of Cambridge. Woodward wrote,

"I should also take this opportunity to emphasize that Professor Longuet-Higgins was thinking along entirely similar lines, and entirely independently developed conclusions very similar to ours."[104]

This statement is not quite true and is certainly not the whole truth. Longuet-Higgins's contributions were not "entirely independent" of Woodward. In the fall of 1964, Longuet-Higgins heard of the scientific problem and learned that its solution used "symmetry arguments based on molecular orbital theory"[195] from Woodward. Absent Woodward's private teachings to Longuet-Higgins, the latter would never applied correlation diagrams to solve the electrocyclization no-mechanism problem. In that sense, Woodward was being generous to Longuet-Higgins. That being said, it was Longuet-Higgins who revealed the value of correlation diagrams to electrocyclizations to Hoffmann via his (Longuet-Higgins's) December 28, 1964, letter[195] to Woodward. Hoffmann subsequently used correlation diagrams to solve independently the cycloaddition no-mechanism problem, and in time to analyze a number of concerted reactions.[15] Given that Woodward used a correlation diagram analysis in his *Aromaticity* essay, and given that it was Longuet-Higgins who first used correlation diagrams for pericyclic reactions – specifically, for and only for electrocyclizations – Woodward could have, likely should have been more forthright regarding credit to Longuet-Higgins. Woodward did not do so. However, in their next joint W–H publication in *Accounts of Chemical Research*,[11] Woodward and Hoffmann properly wrote,

"This was first done by Longuet-Higgins and Abrahamson … "[11]

Third, I speak of Luitzen Johannes Oosterhoff and Egbert Havinga at the University of Leiden,[196,197] Kenichi Fukui at Kyoto University,[198] and R. Stephen Berry (when he was a Yale).[28,30] Given that Woodward presented a historical perspective, naming the three literature precedents to the Woodward-Hoffmann rules would have been appropriate.

Indeed, Woodward did cite Oosterhoff in the *Aromaticity* essay, but his portrayal – for Woodward, the perfectionist[120] – was not quite right. Oosterhoff's orbital symmetry suggestion was not "in a single sentence" in Egbert Havinga and Jos Schlarmann's 1961 publication[196] but in three sentences in two publications; Oosterhoff's suggestion also appeared in a 1963 publication by Havinga as well,[197] though Woodward likely was unaware of this second publication by Havinga. Oosterhoff was also cited in W–H's 1969 treatise in *Angewandte Chemie.*[12] Furthermore, the characterization as "a single sentence" sounds demeaning, especially if that single sentence fully reveals a breakthrough idea.

Fourth, as for Fukui, he was not cited in the *Aromaticity* essay,[104] a compounded error, in that Fukui was not cited in Woodward and Hoffmann's 1965 publication on cycloadditions[4] that included the [4+2] Diels-Alder reaction which Fukui had previously proposed as an orbital symmetry explanation.[198] Woodward and Hoffmann cited Fukui in their fourth *JACS* communication,[6] having been unaware of his precedent in time for it to appear in their second *JACS* communication.[4] Fukui was also cited in their 1969 treatise in *Angewandte Chemie.*[12]

Fifth, Berry was not cited in the *Aromaticity* essay[104] though he was cited in Woodward and Hoffmann's sigmatropic publication[7] and in their 1969 treatise in *Angewandte Chemie.*[12]

Sixth, I cite again Zimmerman's[155–157] and Dewar's[158–160] explanation of allowedness and forbiddenness of pericyclic reactions in terms of the aromatic or antiaromatic (Hückel or Möbius) nature of their transition states. Woodward did not cite either of these research contributions. This omission is ironic and arguably also a shade unprofessional, given that the symposium and the monograph were focused on aromaticity. The W–H rules as presented by Woodward and Hoffmann are silent in terms of aromatic or antiaromatic pericyclic transition states. But the Evans's rules promulgated by Dewar were indeed discussed by Dewar at that symposium and in his chapter in the same monograph.[159] (Was Zimmerman slighted? Likely, but he did not state so in his eight interviews with me. It was complicated for Zimmerman, as he held Woodward in the highest esteem, and he had been a Woodward postdoctoral research fellow.)

Given that one of Woodward's goals for the *Aromaticity* chapter was a historical perspective, a valid criticism is that he could have placed the entire subject within a more generous and accurate historical context.

8. Conclusions

a. On the Advancement of Ideas and Legacies in the Woodward-Hoffmann Publications

In this publication, I have discussed:

- W–H 6NP (Section 4): Hoffmann's draft on "Some Further Selection Rules for Cycloadditions."[70] This draft was composed entirely by Hoffmann. Woodward apparently never responded despite several requests for him to do so by Hoffmann.
- W–H 7 (Section 5): Hoffmann's publication in the *Transactions of the New York Academy of Sciences*. This publication was composed entirely by Hoffmann. There is no evidence that Woodward saw the manuscript before it was published.
- W–H 8NP (Section 6): Hoffmann's "A Catalogue of Concerted Reactions"[116] which was included in early drafts of their 1969 treatise in *Angewandte Chemie* but ultimately deleted by them. This report was composed entirely by Hoffmann. There is no evidence that Woodward saw the "Catalogues" until it was completed and submitted by Hoffmann to be part of another joint W–H publication. It was never used, however.
- W–H 9 (Section 7): Woodward's "The Conservation of Orbital Symmetry,"[104] this being the edited and published text of a lecture he gave in Sheffield, England, in 1966. This publication was composed entirely by Woodward. There is no evidence that Hoffmann saw the essay before it was published.

Beyond the advances in chemistry that were pointed out at the end of each of Sections 4–7, these four writings together provide additional insights.

Three out of these four were authored solely by Hoffmann. His facility for writing and his enthusiasm for publishing was evident by the mid-1960s – all in a language that he did not speak or write effectively until after he was living in America at age 12.

All of the 'unused' chemistry in W–H 6NP eventually found their way into subsequent W–H publications. Yes, Hoffmann was a salvager. But uncharacteristically, the "Catalogue of Concerted Reactions" (W–H 7) was never used in any way (other than in the Supplementary Information of this publication!). Still, the "Catalogue" was very helpful to Hoffmann in his own learning trajectory and proved memorable to his two undergraduate co-workers, Warren J. Hehre and John B. Lisle.

In contrast, Woodward was a model of an anti-salvager. How many of Woodward's possible publications were never written? How many of his students' results lay buried in their theses or postdoctoral reports within the Harvard archives? For example, Woodward's penultimate publication on "The Total Synthesis of Chlorophyll *a*"[199] appeared in a 1990 issue of *Tetrahedron* – 11 years after his death. It was coauthored by 17 of his former students, one of whom (Raymond Bonnett at Queen Mary and Westfield College, London) was self-identified as its author. This full paper followed by 30 years its preliminary publication as a communication.[200]

Woodward's lecture in Sheffield, England, and published as a chapter in a monograph on aromaticity (W–H 9) displays his flair for language.[79,172,174] But it also tells Woodward's W–H origins story, tracing his initial posing of the stereochemical dichotomy at the heart of the electrocyclic reaction story to the vitamin B_{12} synthesis. It is also a demonstration of Woodward's ability (without the help or instruction from or review by Hoffmann, though acknowledged in the publication as Woodward's "partner") to construct MO and perturbation-theory-based arguments for the specific explanation and interconnection, on the orbital level, of many reaction types.

Of course, none of these four writings reaches the scientific breakthrough significance of the first five W–H *JACS* communications of 1965.[3–7] In a sense, the next four writings were place holders. The community had to wait for an avalanche of novel concepts and improved W–H pedagogy that would follow in due course. Those subsequent publications began to flow in 1968 with W–H's essay in the first issue of *Accounts of Chemical Research*[11] and reach their apex in the W–H legacy with the 1969 *Angewandte Chemie* treatise co-written – not just co-authored – by Woodward and Hoffmann, *The Conservation of Orbital Symmetry*.[12,13]

b. On the Nature of the Woodward-Hoffmann Collaboration

I now offer my conclusion and Hoffmann's position about the nature of the Woodward-Hoffmann collaboration (Figure 19). My analysis is based on documentation found in Hoffmann's laboratory notebooks and personal papers, on Woodward's archives at Harvard, on unlimited interviews with Hoffmann, and on Hoffmann's review of advanced drafts of this publication.[201]

First, I look back on their collaboration from May 1964 to August 1965. As discussed in detail in previous publication in this series,[14,24,202,203] there hardly was a W–H collaboration in those years. For their first communication,[3] there is little record of any interaction during Hoffmann's theoretical research (from early May 1964 until mid-October 1964).

Figure 19. The first Cope Awardees, Roald Hoffmann (far left) and R. B. Woodward (far right) with Mrs. Arthur C. (Harriet) Cope and Herman Bloch, then chairman of the board of the American Chemical Society, State Ballroom, Palmer House, Chicago, IL, August 28, 1973. Photograph courtesy of Harvard University Archives.

Ultimately, each wrote their half of the manuscript, Woodward pasted the halves together, and that was that.[14] For their next four *JACS* communications,[4–7] Hoffmann did all the research; Hoffmann wrote the first drafts; Woodward completed them. There is evidence of some face-to-face interactions but very few, just a handful, if that many.[15–17]

Second, regarding the Woodward-Hoffmann collaboration from mid-1965 to mid-1967 – the purview of this report – I conclude that there wasn't much of a collaboration.[83] At least not in the sense that there were multiple interactions, continuous synergistic discussions, frequent dialogue, and co-authored publications (none).

Overall, the limited nature of the Woodward-Hoffmann collaboration during these years (1964 through mid-1967) may seem surprising to many, given that an intimate relationship is implied by the well-known coupled eponym "Woodward-Hoffmann." "Woodward-Hoffmann has long been etched in the minds of the chemists around the world. "Woodward-Hoffmann" seems like one.

I anticipated that Hoffmann would disagree when he first read this conclusion, not so much with the facts as stated above and described in detail in the current and previous publications in this series.[14–17] I anticipated that Hoffmann would disagree with my conclusion, that there was no deeply-intimate Woodward-Hoffmann collaboration in the 1964 to early 1967 period. Because in Hoffmann's memory and with his sensibility, none of it could have happened without Woodward. I anticipated that Hoffmann would remind me of several instances in which Woodward did make critical intellectual contributions, as noted in Hoffmann's laboratory notebook and reported in my previous publications in this series.[14–17] I was right in my anticipations. Hoffmann responded in several email reviews of an advanced draft of this manuscript,

"You're right. I disagree. But you have laid out your argument well."[2]

and

"I think this is a restrictive-to-silly use of the word 'collaboration.' You have informed the reader well about the role Woodward and I had in our joint work. This is not the place to grow restrictive or fussy about what a 'real collaboration' means. It is clear that none of the work would have been done at the time it was done without Woodward talking to Hoffmann and creating ties and situations for continued work, even if I did the work.

"Remember that Woodward posed the original problem to me and provided the frontier orbital solution on electrocyclic reaction [W–H 1[3,14]].

"Think about the Longuet-Higgins letter [of December 28, 1964,[4] in which he informed Woodward of his use of correlation diagrams to solve the electrocyclization mechanism[15]. Our cycloaddition communication [W–H 2[4]] would not have been written without Woodward talking to Longuet-Higgins on one day, and on another day showing the Longuet-Higgins letter to me. That letter set me off running on correlation diagrams and identifying and solving the cycloaddition problem.

> "Recall that Woodward recognized the [3,5] sigmatropic shift was a problem. That observation was critical in my analysis of sigmatropic reactions.[5]

> "Are all these outcomes not the result of a collaboration? Let me answer my last question myself: No, it is not collaboration in the strict sense. Yes, of course, it is collaboration, in the senses that (a) this is the way it goes in science, usually partners making unequal contributions, and (b) you lose a lot in communicating how science really works, how new understanding is created, if you label unequal contributions as indicative of a lack of collaboration."[204]

And separately, Hoffmann concluded,

> "You have traced in great detail the meandering path we actually took. The collaboration was sometimes distant, sometimes closer, and both Woodward and I learned in the process. It was productive. And we and the community gave proper credit to the participants."[205]

As will be revealed in the next publication in this series,[69] the W–H collaboration reached its greatest degree of propinquity[206,207] during the writing of the *Angewandte Chemie* treatise, from mid-to-late 1967 through December 1968.[12] Ironically and importantly, the scientific intimacy between Woodward and Hoffmann was at its maximum when they were furthest separated geographically. (Today, with email and video conferencing, distance is no longer a detriment to scientific collaborations. But in the 1960s, even long-distance telephone calls were expensive, especially intercontinental calls.)

Hoffmann feels strongly and positively about the W–H collaboration and especially favorable toward Woodward.[86] This was publicly revealed in his (Hoffmann's) 2004 essay,[189] in response to E. J. Corey's claim of plagiarism against Woodward.[187,188] Certainly influenced by my numerous interviews with Hoffmann during the past 20 years,[86] I also see Hoffmann's 2004 essay[189] as his very personal validation and attestation of Woodward's contributions to the Woodward-Hoffmann rules and to Hoffmann's own career. Woodward, as well, felt strongly and positively toward Hoffmann.[104,164,165] In addition to their achievements – the Woodward-Hoffmann rules! – what surely matters is how they each felt about each other, and in Hoffmann's case, how he continues to feel. Very strongly and positively toward R. B. Woodward.

Supplementary Information

Roald Hoffmann's unpublished manuscript written in 1966, "A Catalogue of Concerted Reactions."[116]

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