ORBITAL SYMMETRY ANALYSIS OF THE REACTION OF SILYLENES WITH ACETYLENES AND THE DIMERIZATION OF 1-SILACYCLOPROPENES

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Summary

The addition of silylenes to acetylenes, and the dimerization of silacyclopropenes, are treated by Orbital Correspondence Analysis in Maximum Symmetry (OCAMS). The products observed in the latter reaction are consistent with an allowed pathway, a b_{1g} displacement involving rotation of the silacyclopropene molecules relative to one another in the transition state.

A well-known and puzzling mechanistic problem in organosilicon chemistry concerns the reaction between silylenes and acetylenes. At low temperatures silylenes react with acetylenes to form silacyclopropenes [1–3], but at higher temperatures the usual products are 1,4-disilacyclohexa-2,5-dienes [4–6]. Direct $2\pi + 2\pi$ dimerization of silacyclopropene to the six-membered ring was initially suggested as the mechanism [5]. However, this mechanism seemed to be ruled out by the observation that
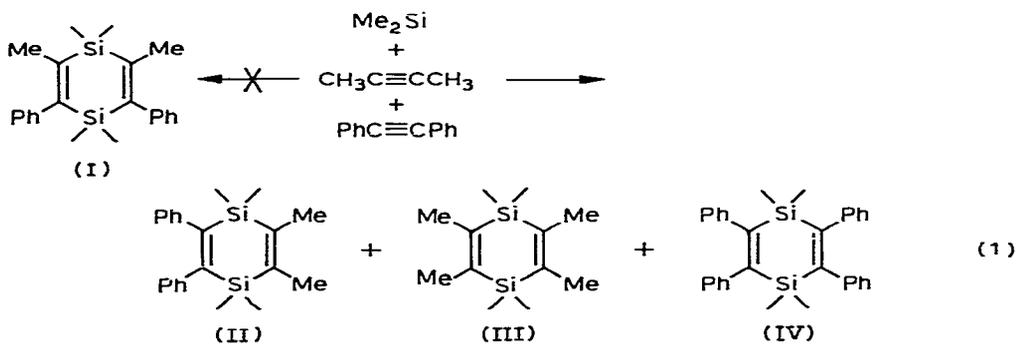
generation of dimethylsilylene in the presence of both 2-butyne and diphenyl-acetylene gave none of the mixed disilacyclohexadiene (I) expected to result from this process. Instead as shown in eq. 1, the reaction produced the other mixed isomer II along with the symmetrical dimers III and IV [6].

Formation of a 1,3-diradical from the original silacyclopropene followed by cross-dimerization would lead to II, but this mechanism was eliminated by the observation that even in the presence of a large excess of diphenylacetylene none of the silacyclopentadiene V was formed (eq. 2). Atwell and Weyenberg therefore

$$(2)$$
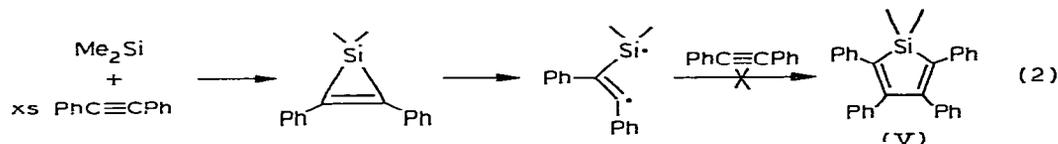
suggested that the dimerization takes place by "a rather specific dimerization of silacyclopropene intermediates" [6].

An alternative mechanism has been suggested by Barton and Kilgour, involving a disilacyclobutene (VI) intermediate [7]. The latter might be generated either by insertion of the silylene into a Si–C bond of a silacyclopropene, or by dimerization of the silylene to form a disilene followed by addition to the acetylene (eq. 3).

$$(3)$$
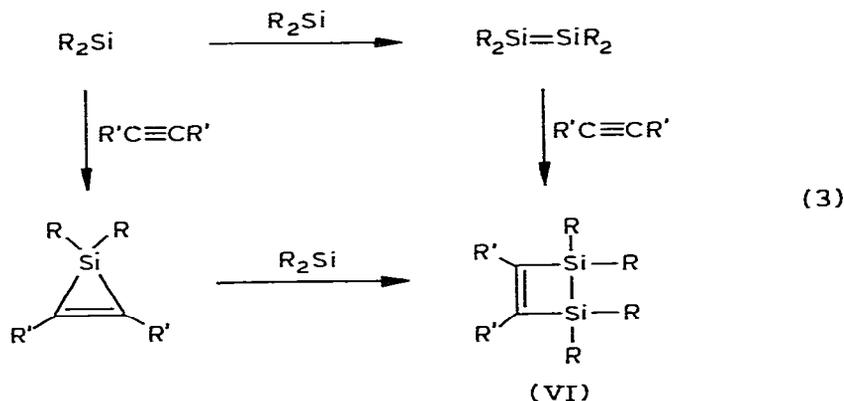
These workers also showed that disilacyclobutene VII reacts with 3-hexyne to produce disilacyclohexadiene VIII, whose regiochemistry is similar to that of II produced in the reaction described earlier (eq. 1).

$$(4)$$
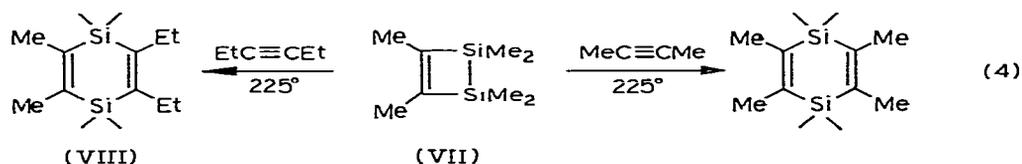
However, the mechanism of Barton and Kilgour has been questioned by Ishikawa et al., who found that silacyclopropene IX dimerizes cleanly to disilacyclohexadienes X and XI at 250°C, even in the presence of a large excess of diphenylacetylene [8]. These workers therefore favored a "direct σ-dimerization" mechanism for the

(5)

(IX)   (X)   (XI)
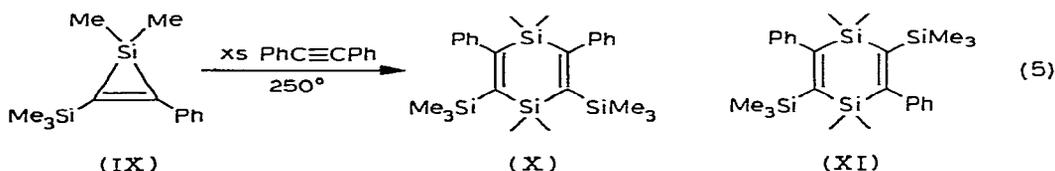
formation of X and XI. There is also evidence that compound IV cannot be formed by the Barton–Kilgour mechanism: When 1,2-diphenyltetramethyl-3,4-disilacyclobutene is heated with diphenylacetylene for 4 h at 350°C, IV is produced in only 1.2% yield [9].

In this paper, we will use symmetry principles to examine the course of three reactions: the addition of silylenes to acetylenes (A); and the dimerization of silacyclopropenes, by both concerted (B) and stepwise (C) mechanisms.

It should be obvious that a simple classification of the various possible reactions as either "allowed" or "forbidden" by symmetry would be inadequate. A "symmetry forbidden" reaction is indeed expected to have a high activation energy, but not necessarily one that is prohibitive at 200°C and above. A more useful approach would be one which compares the relative ease of alternative reaction pathways in terms of the symmetry-breaking properties of their reaction coordinates. This is the rationale of Orbital Correspondence Analysis in Maximum Symmetry (OCAMS) [10–12], which will now be applied to the reactions under considerations. The relation of this method to the more familiar orbital correlation procedure of Woodward and Hoffman [13] (W.-H.) is illustrated in the ensuing discussion of reaction A.

A. Cycloaddition of dimethylsilylene and acetylene

Figure 1 can be regarded as a W.-H. orbital correlation diagram that has been expanded into an OCAMS correspondence diagram. The two reactant molecules are oriented so as to conform to the C_{2v} symmetry of the product. On either side, the system has three non-trivial symmetry elements: an axis of rotation, C_2, and two perpendicular mirror planes, m and m'. These are more rigorously specified, according to the axis convention at the upper right of Fig. 1, as $C_2(z)$, σ_{yz} and σ_{xz} respectively. Temporarily following Woodward and Hoffmann [13], we retain the first two, which bisect the π_z-bond that is broken in the reaction, and disregard m', which does not, as unimportant. π_y and π_y^*, which survive the cycloaddition unchanged, need not have been included in the diagram at all. The remaining four orbitals on the left are connected by correlation lines with those on the right which have the same symmetry properties with respect to the two "important" symmetry elements. In the ground state reaction, the doubly occupied π_z (SS) and σ_+ (SS) intercorrelate, but sp_z^2 (SS), which is doubly occupied in the singlet ground state of $(CH_3)_2Si$ [14], correlates with the vacant σ_+^* (SS) rather than with the occupied σ_- (AA). The ground state cycloaddition is therefore "W.-H. forbidden".

Up to this point, OCAMS follows an identical track. Two formal differences between the methods, which will turn out to have important consequences in the more complicated reactions to be dealt with later on, are inconsequential in the context of our simple example: (1) Characterization of each MO by its irreducible representation in C_{2v} is equivalent to specifying its symmetry with respect not only
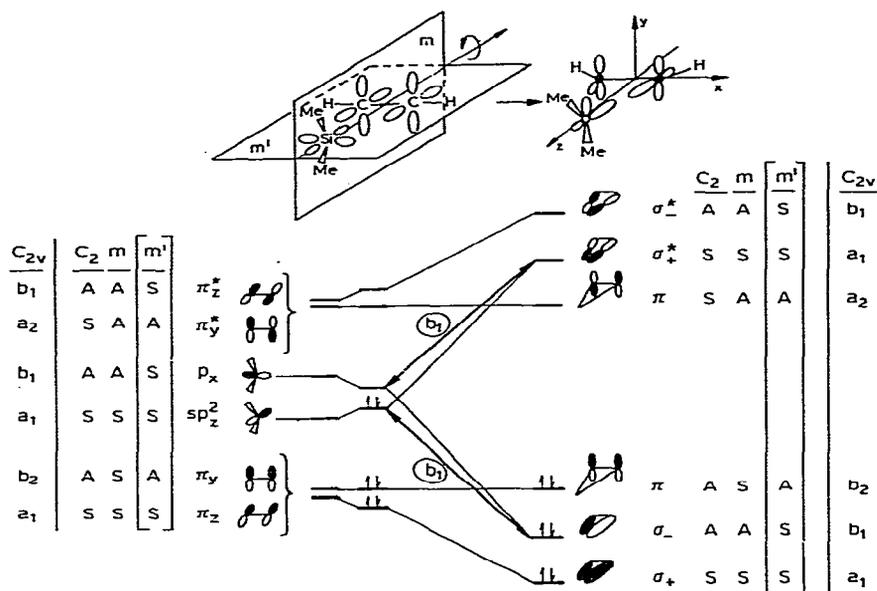
Fig. 1. Woodward–Hoffmann correlation diagram (OCAMS Correspondence Diagram) for cycloaddition of dimethylsilylene to acetylene.

to C_2 and m, but to m' as well. As long as this latter symmetry element exists, the distinction between σ- and π-orbitals is maintained. For this reason m' has been assigned mechanistic importance in photochemical reactions [15]. Its explicit inclusion is, however, unnecessary, because the irreducible representation of an orbital in C_{2v} is fully determined by its behavior with respect to C_2 and m, or, for that matter, either of them and m'. (2) π_y is not intuitively excluded as "not involved in the reaction". Although its omission in the present case would have been harmless, it will be clear from subsequent examples that valuable mechanistic information can sometimes be discarded along with orbitals that are apparently not implicated in the reaction under consideration.

The W.-H. correlation lines, now renamed "direct correspondences", are the same as before. They represent the orbital correlations which would obtain if the reaction were forced to follow a reaction path that retains C_{2v} symmetry. The "forbidden-ness" of such a pathway results, as before, from the absence of a direct correspondence between two doubly occupied orbitals: sp_z^2 (a_1) and σ_- (b_1). OCAMS now goes on to inquire whether a convenient pathway of lower symmetry exists, whereby these two offending orbitals can be induced to intercorrelate. Formally, in order to induce a $a_1 \leftrightarrow b_1$ correspondence, the system must be distorted along a b_1 symmetry coordinate, because $a_1 \times b_1 = b_1$. This requirement can be expressed in W.-H. parlance as follows: in order to interrelate two orbitals with different symmetry properties, the symmetry of the system is reduced so that the only symmetry elements remaining are those with respect to which both orbitals have identical symmetry labels. In Fig. 1, sp_z^2 and σ_- have only their label with respect to m' (S) in common, so this symmetry element is the only one that can be retained along an "allowed" pathway.

An off-axial approach of $(CH_3)_2Si:$, oriented so that the occupied hybrid orbital and one lobe of the vacant p_z orbital are both directed towards π_z, has the correct symmetry properties, which can be expressed in either of two equivalent ways: (1) the molecules approach one another along a b_1 symmetry coordinate in C_{2v}; (2) symmetry is reduced along the reaction pathway from C_{2v} to C_s^{xz}, in which m' $(=\sigma_{xz})$ is the only non-trivial symmetry element retained. It follows that the cycloaddition reaction, although "W.-H. forbidden", is predicted by OCAMS to be "allowed" along a b_1 pathway, as computations on the analogous $[^1CH_2 + \text{ethylene}]$ cycloaddition amply confirm [16,17].

B. Concerted dimerization of silacyclopropenes

Figure 2 is the correspondence diagram for concerted dimerization of silacyclopropene. The product can be taken to be planar, with D_{2h} symmetry, so the two reacting molecules are set up in the same symmetry point group. The orbitals are stacked energetically in the usual manner: the energy increases with the number of nodal surfaces; σ-orbitals are more bonding and σ^*-orbitals more antibonding than are π- and π^*-orbitals, respectively.

The four bonding and four antibonding orbitals on either side span the eight
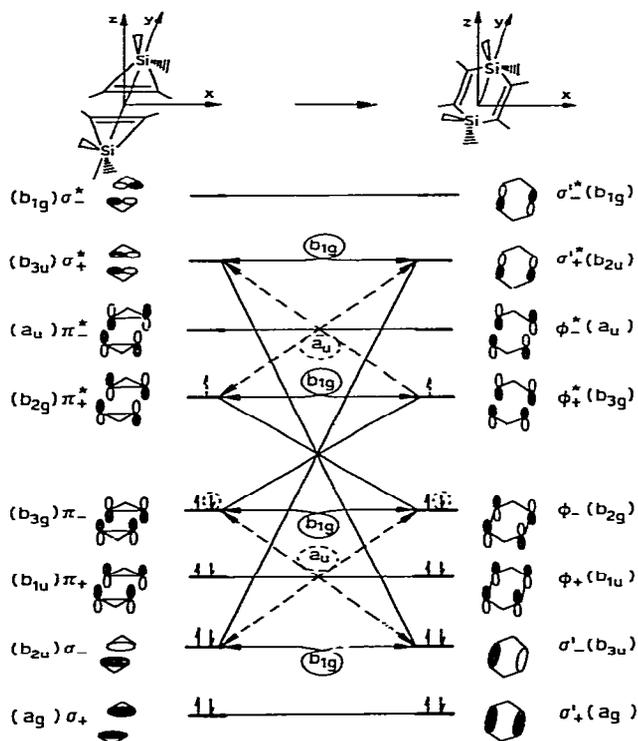
Fig. 2. Correspondence diagram (D_{2h}) for concerted dimerization of dimethylsilacyclopropene. (The full and dashed two-headed arrows represent the correspondences induced by b_{1g} and a_u displacements, respectively.)

irreducible representations of D_{2h}, so the direct correspondences are unique. At least three symmetry operations are required in order to describe these MOs fully using the conventional S,A-notation [12a], so it is simpler to adhere to group theoretical nomenclature. Two direct correspondences between bonding and antibonding orbitals $\sigma_- \leftrightarrow \sigma'^*_+$ and $\pi_- \leftrightarrow \phi^*_+$, "forbid" dimerization, and its converse, thermal fragmentation of the dimer, along a totally symmetric (a_g in D_{2h}) symmetry coordinate. Of these, only the former blocks photochemical fragmentation of the dimer, which one would presume to occur on the potential energy surface of the first excited singlet or triplet. This is because the one-electron correspondences between the pairs of π-orbitals, $\phi_- \leftrightarrow \pi^*_+$ and $\phi^*_+ \leftrightarrow \pi_-$, are direct.

In order to "allow" the photochemical reaction, a correspondence has to be induced between $\sigma_- (b_{2h})$ and $\sigma'_- (b_{3u})$; clearly, distortion of the system along a b_{1g} ($= b_{2u} \times b_{3u}$) coordinate is called for. We note, moreover, that a b_{1g} distortion also induces the correspondence between the HOMOs $\pi_- (b_{3g})$ and $\phi_- (b_{2g})$, so it "formally" also allows the ground state reaction, in both directions. A b_{1g} pathway is one that retains all the symmetry elements with respect to which a b_{1g} molecular orbital, for example σ^*_- and σ'^*_- at the top of Fig. 2, are symmetric. These are easily confirmed to be: $C_2(z)$, $\sigma_h(xy)$, and i (inversion) which, along with the identity element, E, comprise the symmetry point group, C^z_{2h}. A b_{1g} distortion thus reduces the symmetry from D_{2h} to its subgroup, C^z_{2h}, which is termed the kernel of the irreducible representation b_{1g} of the original group [11a].

There is, however, another way of formally allowing the ground-state reaction. An a_u distortion is capable of inducing two $\pi \leftrightarrow \sigma$ cross-correspondences between doubly occupied MOs: $\sigma_- (b_{2u}) \leftrightarrow \phi_- (b_{2g})$ and $\pi_- (b_{3g}) \leftrightarrow \sigma'_- (b_{3u})$. A pathway which proceeds along an a_u reaction-coordinate, retains the symmetry elements of its kernel, D_2, i.e., [E, $C_2(z)$, $C_2(y)$, $C_2(x)$].

Two modes of symmetry reduction from D_{2h} have to be considered as possible "allowed" pathways for dimerization. Since correspondence (and correlation) diagrams can be read in either direction, such pathways will also be "allowed" for dimer fragmentation: (1) a_u, implying D_2 symmetry, legitimate only for the thermal reaction; (2) b_{1g}, leading to C^z_{2h}, which "allows" both the thermal and photochemical processes. The geometric nature of these coordinates is illustrated in Fig. 3, along with several other D_{2h} symmetry coordinates of the pair of silacyclopropene molecules, to which reference will be made later on.

The off-perpendicular approach along the y-axis, with retention of D_2 symmetry, is analyzed on the left side of Fig. 4, where it is referred to as Mode 1. The MOs of the monomer pair at the extreme left and those of the dimer in the center are simply those of Fig. 2. Both sets are respecified according to the irreducible representations of D_2; the shifts in orbital energies schematically reflect the interactions between pairs of orbitals that have the same irreducible representation in the subgroup. The D_2 symmetry labels are derived from those of D_{2h} by ignoring the distinction which no longer exists, between g and u.

We note in the diagram for Mode 1 that reduction of symmetry from D_{2h} to D_2 stabilizes all of the bonding orbitals and destabilized all of the antibonding orbitals. This happens because elimination of $\sigma_{x,y}$ brings each occupied σ orbital into the same representation as an empty π-orbital, and vice versa, so that each occupied orbital is stabilized by $\sigma-\pi$ mixing. The stabilization of all the bonding MOs of the monomers in the D_2 orientation suggests that the axial, noncoplanar approach should be more

D_{2h} Kernel subgroup

① a_u D_2

② b_{1g} C_{2h}^z

③ b_{1u} (towards "boat") C_{2v}^z

④ b_{3g} (towards "chair") C_{2h}^x

⑤ b_{2g} C_{2h}^y
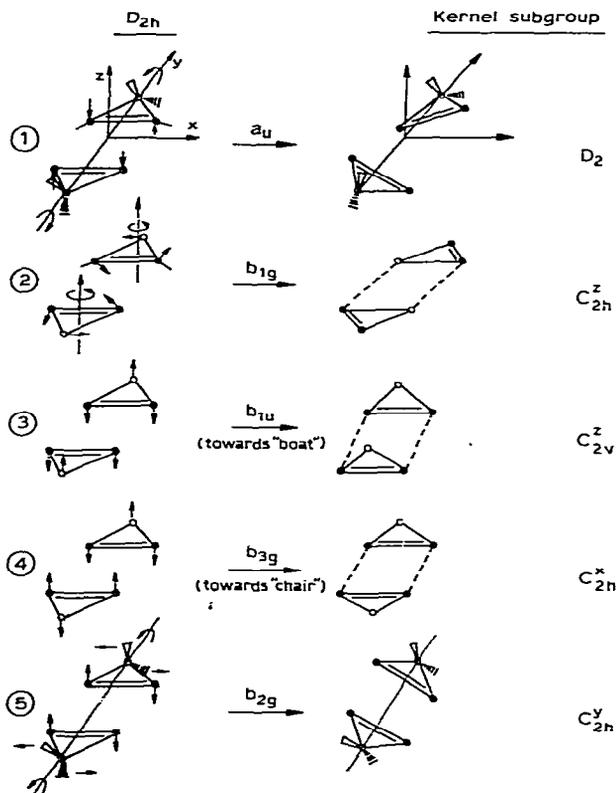
Fig. 3. Symmetry reduction below D_{2h} along various symmetry coordinates.

D_{2h} — a_u → D_2 ← a_u — D_{2h} — b_{1g} → C_{2h}^z ← b_{1g} — D_{2h}

mode 1   I   or   II   mode 2

$(b_{1g})\sigma_-^*$ — (b_1) — (b_1) (a_g) — (a_g) — $\sigma_-^*(b_{1g})$

$(b_{3u})\sigma_+^*$ — (b_3) — (b_2) $\sigma_-^*(b_{1g})$ (b_u) — (b_u) — $\sigma_+^*(b_{3u})$

$\cdot(a_u)\pi_-^*$ — (a) — (a) $\sigma_+^*(b_{2u})$ (a_u) — (a_u) — $\pi_-^*(a_u)$

$(b_{2g})\pi_+^*$ — (b_2) — (b_3) $\phi_-^*(a_u)$ (b_g) — (b_g) — $\pi_+^*(b_{2g})$

$\phi_+^*(b_{3g})$

$(b_{3g})\pi_-$ — (b_3) — (b_2) $\phi_-(b_{2g})$ (b_g) — (b_g) — $\pi_-(b_{3g})$

$(b_{1u})\pi_+$ — (b_1) — (b_1) $\phi_+(b_{1u})$ (a_u) — (a_u) — $\pi_+(b_{1u})$

$(b_{2u})\sigma_-$ — (b_2) — (b_3) $\sigma_-(b_{3u})$ (b_u) — (b_u) — $\sigma_-(b_{2u})$

$(a_g)\sigma_+$ — (a) — (a) $\sigma_+(a_g)$ (a_g) — (a_g) — $\sigma_+(a_g)$
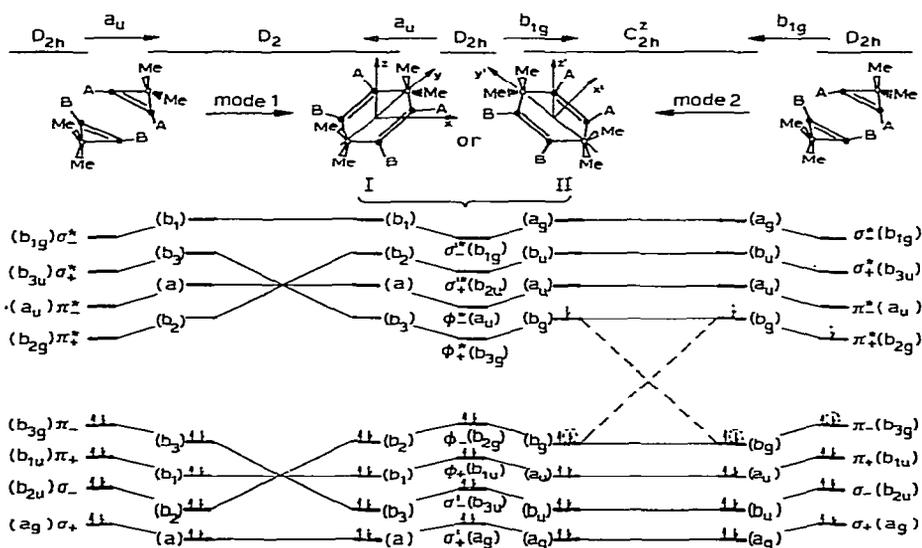
Fig. 4. Correspondence (correlation) diagrams along the two "OCAMS-allowed" pathways for dimerization to 1,4-disilahexadiene-2,5. Mode 1 (D_2), across the C=C double bonds; Mode 2 (C_{2h}), across a pair of C–Si bonds (the additional asymmetry introduced by the substituents is ignored.)

facile than one which retains coplanarity *. (By a similar argument, it might be supposed that the dimer would also be more stable in D_2 than in D_{2h}, but such a tendency would be opposed, and probably dominated, by stereoelectronic constraints.)

The lines in the left half of Fig. 4 all represent direct correspondences in D_2 symmetry, and faithfully reproduce the a_2-induced correspondences and the remaining direct D_{2h} correspondences of Fig. 3. The Mode 1 half of Fig. 4 can thus be regarded as being a W.-H, correlation diagram, since one of the three rotational axes retained, $C_2(y)$, bisects the σ- and π-bonds of the reactant, and another, $C_2(x)$ bisects those of the product. A concerted metathesis of the σ- and π-bonds by this mechanism is thus allowed by both methods of analysis. The product of reaction along this pathway is necessarily Dimer I, in which two substituents that were originally present in a single acetylene molecule find themselves flanking each of the silicon atoms. As has been noted above, the isomer distribution observed in the products of reactions with suitably substituted acetylenes [6] shows that Mode 1, though formally "allowed", does not occur. Evidently, the simultaneous rupture and formation of four bonds is too costly a process, and the reaction prefers to take an energetically more economical course.

The alternative course "allowed" by OCAMS, a b_{1g}, in-plane, relative displacement of the two monomers, appears as Mode 2 at the right of Fig. 4. Again, all the correspondences are direct, producing a C_{2h}^z correlation diagram. If the b_{1g} displacement depicted as (2) in Fig. 3., i.e., simultaneous rotation of both reactant molecules – each about its own z-axis, is now allowed to occur, two C–Si single bonds will face one another in the C_{2h}^z geometry suitable for the energetically less costly formation of the dimer as substitutional isomer II. This energetically favored OCAMS-allowed pathway is consistent with the experimental results [6,19].

It should be emphasized that although all the correspondences at the right side of Fig. 4 are direct, the correspondence diagram of Mode 2, unlike that of Mode 1, is not a Woodward-Hoffmann correlation diagram, because none of the symmetry elements of C_{2h}^z bisects any of the bonds made or broken. If, however, the orbital symmetry analysis were to be discounted on these grounds, and the experimental results rationalized solely in terms of the greater ease of breaking two C–Si single bonds than two C=C double bonds, another question arises: Why is the 1,4-disilahexadiene-2,5 formed exclusively, whereas the formation of 1,2-disilahexadiene-3,5, which would appear to be no less thermodynamically stable, is not observed at all?

Figure 5 is an OCAMs correspondence diagram for dimerization to the latter product. The direct correspondences, which in this case can be regarded as W.-H. correlations, since two of the symmetry elements C_2^z and $σ_{xy}$ bisect the new Si–Si and C–C σ-bonds, show the reaction to be forbidden in total (C_{2v}) symmetry. OCAMS then goes on to show that a correspondence between $σ_-(b_1)$ and $σ'_-(a_1)$ is called for in order to "allow" the ground state dimerization. Such an in-plane distortion would, however, take the reactant molecules away from their proper mutual orientation, so this mode of dimerization would not be expected to occur.

It might be noted in passing that photochemical fragmentation of 1,2-disilacyc-

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* In the perpendicular D_{2d} orientation, b_1 and b_3 orbitals are degenerate, and would be split by a "pseudo-Jahn-Teller effect" [18], regenerating D_2.
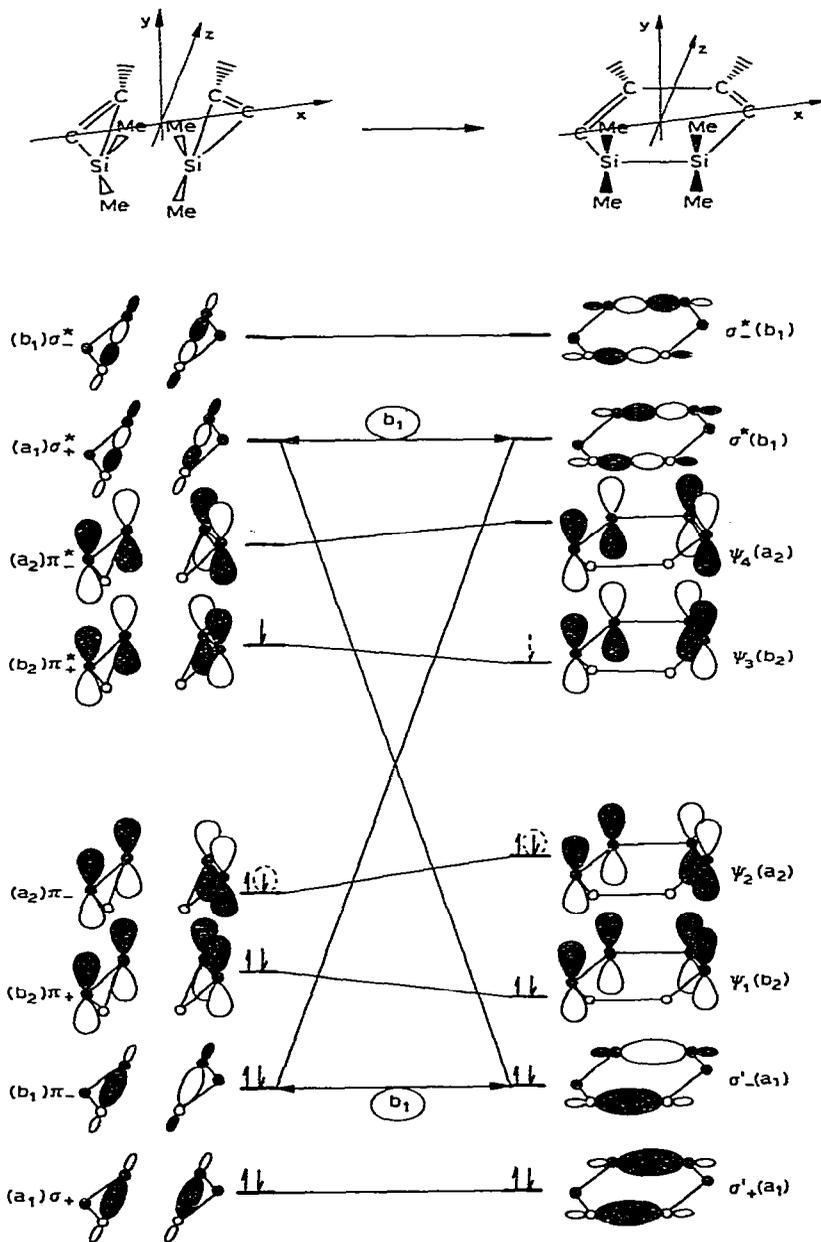
Fig. 5. Correspondence diagram (C_{2v}) for "OCAMS-forbidden" dimerization to 1,2-disilahexadiene-3,5.

lohexadiene-3,5 would also be prevented by the mutual incompatibility of the same two MOs. In line with this expectation, the photoreactions of derivatives of this molecule do indeed take quite a different course [20].

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C. Stepwise dimerization of silacyclopropene

The fact that Mode 1 of Fig. 3, "allowed" by both W.-H. and OCAMS, does not occur, presumably too many bonds must be broken and remade at once, suggests that stepwise mechanisms leading to this product cannot be overlooked. Of these, probably the simplest is the sequence comprising a $[_\pi 2_s +_\pi 2_s]$ cycloaddition to a disilatricyclohexane, followed by a $[_\sigma 2_s +_\sigma 2_s]$ cycloreversion. Both steps of this mechanism, which has been suggested by Gilman et al. [5], are "W.-H.-forbidden" [13b]; OCAMS rejects it on rather more elaborate grounds, as follows.

Figure 6 consists of a pair of correspondence diagrams, in which only the bonding orbitals directly involved in each step are drawn along with their antibonding counterparts. As justified at some length elsewhere in connection with the similar thermal dimerization of cyclobutadiene [12b], the tricyclic product is drawn for convenience in the planar D_{2h} geometry. From this highly strained conformation, the molecule can be stabilized by bending in one of two ways: (a) along a b_{1u}
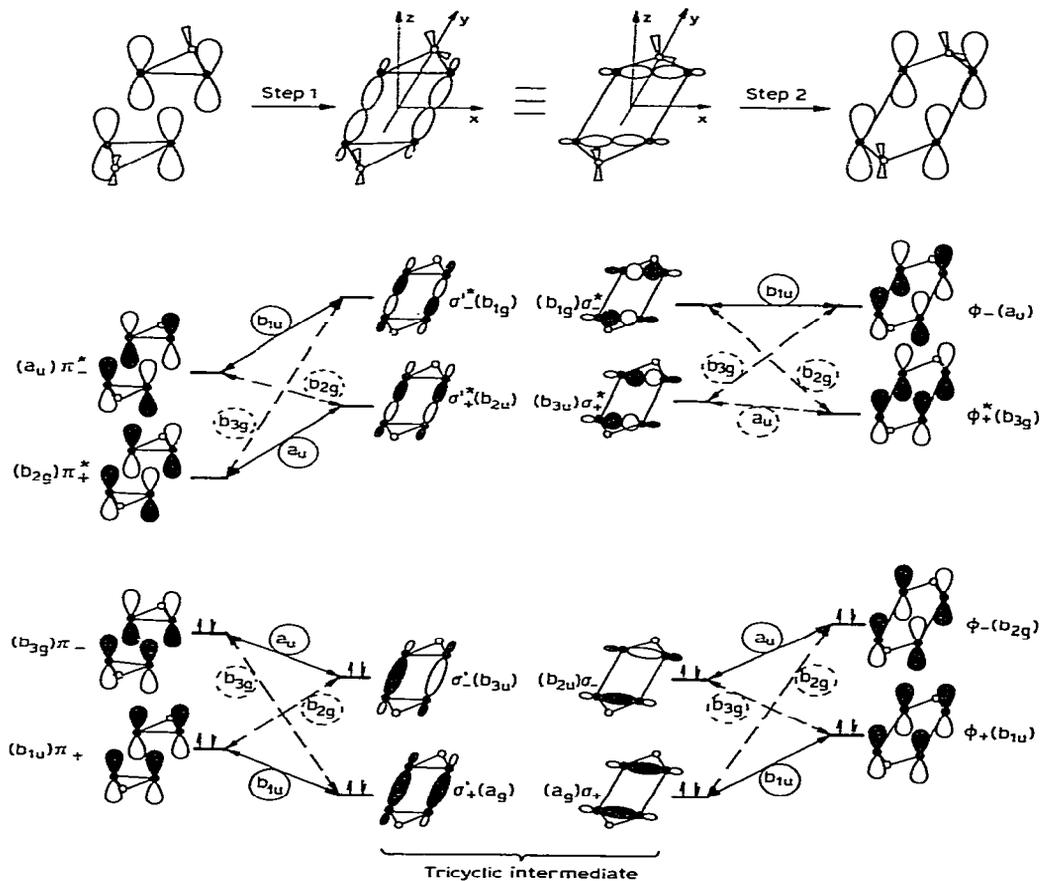
Fig. 6. Correspondence diagrams (D_{2h}) for Gilman's stepwise dimerization mechanism. Step 1: $[_\pi 2_s +_\pi 2_s]$ cyclodimerization of dimethylsilacyclopropene. Step 2: $[_\sigma 2_s +_\sigma 2_s]$ cycloreversion of tricyclic intermediate.

coordinate, such as (3) of Fig. 3, into the boat conformation (C_{2v}^-); (b) along a b_{3g} coordinate, like (4) of Fig. 3, to the chair configuration (C_{2h}^x).

Figure 6 shows that Step 1 can proceed "allowedly" in one of two ways, each of which is a superposition of two symmetry coordinates: (a) $[b_{1u} + a_u]$ or (b) $[b_{3g} + b_{2g}]$. The first of these modes of reaction includes b_{1u}, and so necessarily leads to the boat. In addition, however, it calls for an a_u coordinate, such as (1) of Fig. 3. It follows that a near-perpendicular, D_2, approach followed by bending into the boat conformation is an "allowed" pathway for Step 1. If, as might be expected, the tricyclic intermediate is strained in this conformation, the reverse of Step 1 should also be facile. The b_{3g} component of the alternative pathway leads as naturally to the chair conformation, but the superposition on it of a b_{2g} motion is also prescribed. Unlike the a_u twist, which is a relative reorientation of the two monomer molecules, a b_{2g} coordinate can be either a simple overall rotation of the two moieties, which does not change the potential energy of the system and is thus ineffective [11], or else includes a twist of the $Si(Me)_2$ groups of both monomers, like (5) of Fig. 3, which raises the energy of activation gratuitously. Formation of the chair form of the tricyclic intermediate is thus disfavored.

Step 2, i.e., generation of the plane-symmetric 1,4-disilahexadiene-2,5 from the tricyclic intermediate once more calls for a composite displacement in D_{2h}. Since Step 1 is predicted to occur preferentially via the boat form, $[b_{3g} + b_{2g}]$ is clearly unsuitable, and only $[b_{1u} + a_u]$ need be considered. The totally symmetric (a_1) coordinate of C_{2v}^-, which regenerates the planar geometry of the product, is of symmetry species b_{1u} in the higher D_{2h} symmetry of the product. To this, however, must be added an a_u component (a_2 in C_{2v}). This can no longer be a simple reorientation of two monomers, but is rather a skeletal distortion of the six-membered ring and, as such, is energetically costly, perhaps prohibitively so.

The OCAMS conclusions regarding the Gilman mechanism may be summarized as follows: the formation of the chair intermediate is blocked at Step 1. That of the boat form is allowed, but its fragmentation to the monomers should be much more facile than Step 2. Evidently, if an alternative convenient pathway for dimerization exists, it will be taken in preference. The Gilman mechanism would therefore not be expected to compete effectively with Mode 2 of Fig. 4.

Conclusions

Following the OCAMS approach, we have determined the symmetry coordinates along which the reacting system must be distorted in order to "allow" reactions A, B and C. An assessment of the energetic consequences of the distortions formally prescribed by OCAMS in each case provides important insights into the mechanism which do not appear when the Woodward–Hoffmann formalism is followed.

Thus, Reaction A, the cycloaddition of dimethylsilylene to acetylene is adjudged to be facile, even though a strict axial approach is formally "forbidden". Reaction B, the concerted dimerization of the resulting silacyclopropene, is shown to lead preferentially to 1,4-disilahexadiene-2,5 via a C_{2h} transition state involving simultaneous rupture and re-formation of two symmetrically disposed C–Si bonds. In contrast Reaction C, stepwise dimerization of silacyclopropene, is rejected on the basis of the excessive energetic requirements of distortion along the symmetry coordinates formally prescribed by OCAMS.

It must be borne in mind, however, that the mechanism selected above is not the only one which is compatible with OCAMS. Both steps in the mechanism suggested by Barton and Kilgour [7], consisting of a presumably conrotatory disilacyclobutene–disilabutadiene cycloreversion followed by a $[_\pi4_s + _\pi2_s]$ cycloaddition, are "allowed" by OCAMS [12c,d] as they are by Woodward and Hoffmann [3c,d] and do not seem to impose excessive energetic demands.

If two pathways for the formation of disilacyclohexadienes from silylenes and acetylenes are feasible, which one actually occurs? The evidence is incomplete at present, but it seems possible that either pathway can be followed, depending on the substitution in the silacyclopropene ring. The results reported by Ishikawa and coworkers strongly suggest that direct dimerization of some silacyclopropenes takes place [8]; we believe that this is most likely to occur according to Mode 2 of Fig. 4. On the other hand, evidence indicates that some silacyclopropenes do not thermolyze to give disilacyclohexadienes, but instead decompose by other thermolytic pathways [1,2]. The case of tetramethylsilacyclopropene is especially relevant. When dimethylsilylene is generated in the presence of 2-butyne at high temperature, the product is disilacyclohexadiene (III) [6]. However, according to Conlin and Gaspar, tetramethylsilacyclopropene does not dimerize to III upon heating [1]. Thus the formation of III apparently does not take place via dimerization, but may instead be formed by the Barton–Kilgour mechanism.

Acknowledgement

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Note added in proof. A referee has pointed out that simple perturbation theory and second-order Jahn-Teller considerations would also predict a b_1 pathway for the formation of silacyclopropene and a b_{1g} pathway for its dimerization, since these are the symmetry species of the lowest excited states of the products of the respective reactions and should therefore be those of the preferred decomposition modes. (See Chapter I of R.G. Pearson, Symmetry Rules for Chemical Reactions, Wiley, N.Y., 1976.) These predictions do agree with those of OCAMS, but only because all of the non-correlating occupied orbitals in Figs. 1 and 2 are brought into pairwise correlation by the same symmetry-reducing distortion which couples the HOMO with the LUMO. It cannot be expected that this will always be the case.