Scheme XVI

volvement of tight ion-pair intermediates 11.

The balance between 2 and 11 as well as between 11 and 12 is rather delicate and should be subject to the effects of the medium and nature of the reagent. The addition of strong electrolytes can result in (i) the shift of an intermediate structure toward a more polar one (2 → 11 or 11 → 12) and (ii) the transformation of an ion pair 12 into other ion pairs (e.g., 37) due to anion exchange in ion pairs. The formation of covalent perchlorates 36 (Scheme XV) seems to prove the importance of this process. The use of polar solvents (like HCOOH) or solvents capable of the specific solvation of Cl⁻ (like SO_2) appears to be especially favorable for the stabilization of solvent-separated ion pairs, and the net result of RSCl addition under these conditions can be very close to the reactions involving "bare" ESIs. This consideration allows the suggestion of a general mechanism for the reactions discussed covering the

whole spectrum of polarity conditions (Scheme XVI).

The above considerations leave some aspects of the discussed mechanism unanswered. One of the most important of these is the problem of the possible pathways for the transformation of a σ-sulfurane or tight ion pair into an adduct with trans stereochemistry. This problem has been briefly discussed in the literature[17,36,52] but requires special theoretical analysis and additional experimental studies.

Conclusion

In conclusion, we wish to make several comments on the general methodology of organic mechanism investigations. In our opinion the creation of a concise mechanistic picture necessitates solving two basic problems: (i) experimental studies of the reactivity of the extreme alternative intermediates under conditions identical or sufficiently close to the real ones used in the reactions; (ii) elaboration of clear-cut experimental criteria which will allow in-between intermediate species to be identified. Thus, we are sure that the long discussed problem of the involvement of such cyclic intermediates as halonium[3,4] or mercurinium[4,26b] ions in Ad_E processes cannot be unequivocally solved without direct experimental studies of the reactivity of these species. At the present time such an approach is viable, and we believe that in this paper its fruitfulness has been demonstrated both for the analysis of mechanistic problems and for the extension of the synthetic utility of Ad_E reactions.

The 1,2 Hydrogen Shift: A Common Vehicle for the Disappearance of Evanescent Molecular Species

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Received February 9, 1979

Chemistry is intellectually challenging because it is constantly changing. One of the most pervasive examples of this metamorphosis is the manner in which "highly unstable intermediates" have a way of becoming rather well-characterized chemical species. One such example is trimethylenemethane, $C(CH_2)_3$. For many years considered a figment of the theorist's imagination,[1] trimethylenemethane is now becoming the focus of a number of experimental studies,[2] which have established conclusively[3] the triplet nature of the electronic ground state. More generally the entire classes

of carbenes,[4-7] nitrenes,[8] and vinylidenes[9] have in recent years come to the forefront of chemical research.

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Highly unstable intermediates can be exceptionally worthwhile subjects for theoretical study. This is because careful theoretical predictions for such evanescent species are generally just as reliable as the analogous predictions for stable, closed-shell ground-state molecules. As noted above, carbenes, nitrenes, and vinylidenes are three related molecular families which are quite difficult to characterize in the laboratory. In fact the very short lifetimes (practically all under 1 s[10]) of carbenes, nitrenes, and vinylidenes are perhaps their most characteristic property. One reason for these very short lifetimes is that most of these divalent species are subject to rapid rearrangements, i.e., isomerization reactions. The most common rearrangement reaction of carbenes is the 1,2 shift of a hydrogen, generating an alkene.[11] It should be noted, of course, that the simplest carbenes (CH_2 and the halocarbenes CHX and CXY) and nitrenes (NH and the halonitrenes NX) are not subject to the 1,2 hydrogen shift. In fact the most fundamental difference between alkylcarbenes and CH_2 (or CBr_2) is that the alkylcarbenes undergo isomerizations which are often so rapid as to preclude[12] the additions to multiple bonds and insertion reactions which are so common for CH_2.

Experimental Perspective

For alkylcarbenes, the 1,2 hydrogen shift is of the general form

$$R_aR_bHC-\ddot{C}R_c \rightarrow R_aR_bC=CR_cH \qquad (1)$$

One of the earliest studies of this reaction which was recognized as such was the work of Friedman and Shechter[13] in 1959. They found, for example, that isopropylcarbene isomerizes to yield chiefly propylene and that the primary product of the methylethyl-carbene rearrangement is the cis isomer:

$$\qquad (2)$$
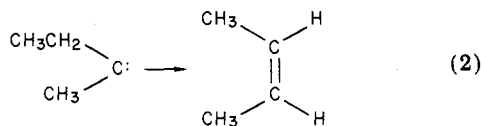
The simplest example of reaction 1 is the methyl-carbene–ethylene isomerization:

$$H_3C-\ddot{C}H \rightarrow H_2C=CH_2 \qquad (3)$$
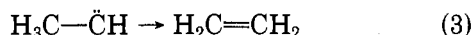
This reaction was studied in the middle 1960's by the groups of Frey[12,14] and Kistiakowsky[15] via the photolysis of both diazoethane[14,15] ($CH_3-CH=N^+=N^-$) and methyldiazirine,[12]

1
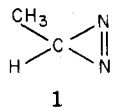
Although acetylene was also observed as a product, this was shown to arise from excited ethylene and not methylcarbene itself.

Since 1959 there have been a sizeable number of experimental studies of carbene hydrogen migrations.[12-44] It is reasonable to ask the question "what have we learned concerning the 1,2 hydrogen shift from these laboratory studies?" One of the most basic understandings[38] to emerge is that the hydrogen migration occurs on the singlet potential-energy surface. A series of studies, by Kirmse and Buschhoff,[25] by Moritani, Yamamoto, and Murahashi,[26] and by Sohn and Jones,[32] have led to this conclusion. 1,2 alkyl shifts also occur via the singlet state, while 1,2 phenyl migrations appear possible[33] on the triplet potential surface. In this light, it should be noted that the ordering of rates of 1,2 migrations was established as early as 1961 by Phillip and Keating[19] as being hydrogen > phenyl > methyl.

Prior to 1970, it was generally held[10,11] that systems allowing a 1,2 migration were quite unlikely to yield the cyclopropane product characteristic of singlet methylene additions to olefins:

$$\qquad (4)$$
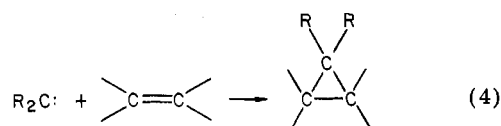
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The few exceptions to this rule were typically highly unsaturated species, for which the intramolecular rearrangements of the carbene in solution either could not occur, or proceeded at a rate comparable to that of (4). However, this line of reasoning was dealt a severe blow by the 1970 paper of Moss and Mamantov[29] concerning methylchlorocarbene. Moss and Mamantov found that methylchlorocarbene added to a variety of olefins to give the anticipated cyclopropanes. Thus it is apparent that the rate of the 1,2 hydrogen shift for methylchlorocarbene is drastically curtailed relative, for example, to methylcarbene, which adds to propene but not to higher alkenes.[12,14,15] Nevertheless, Moss and Mamantov did observe under the same conditions (photolysis of methylchlorodiazirine in the presence of olefins) the 1,2 hydrogen shift to vinyl chloride (eq 5).

$$\tag{5}$$
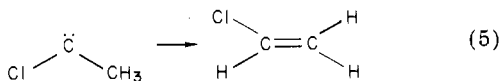
They conclude that the addition (eq 4) and rearrangement (eq 5) products are formed in roughly comparable yields.

Several more recent experimental studies[32,35,42] have dealt with the general problem of suppressing the 1,2 hydrogen shift, for at least long enough to observe cyclopropane products. In a very important paper, Sohn and Jones[32] reasoned that triplet carbenes might not undergo this intramolecular rearrangement. Sohn and Jones were in part guided by the suggestion of Moritani, Yamamoto, and Murahashi[26] that hydrogen migration to triplet carbenes must mimic the unknown 1,2 shift in free radicals. Sohn and Jones found the direct photolysis of methyl diazopropionate to yield as major product methyl acrylate, resulting from the 1,2 hydrogen shift

$$\tag{6}$$
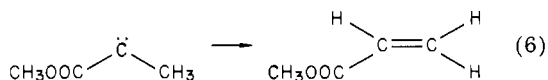
However the benzophenone-sensitized decomposition, designed to eliminate the singlet carbene, did in fact yield the desired cyclopropane product in 72% yield. This direct demonstration of the inability (or at least reduced ability) of triplet carbenes to undergo the 1,2 H shift is certainly a beautiful example of innovative carbene chemistry.

A topic of much recent interest is the stereochemistry of the carbene 1,2 hydrogen shift. Although our general strategy is to defer discussion of theoretical papers to the latter sections of this Account, the pioneering work of Hoffmann, Zeiss, and Van Dine (HZV)[45] must be mentioned at this point. Blending chemical intuition with semiempirical MO theory, HZV predicted that the hydrogen which migrates, labeled H_m (eq 7), is that

$$\tag{7}$$

1
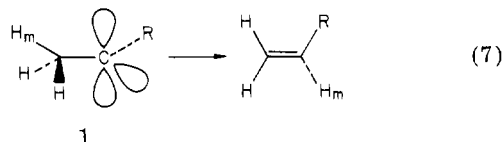
which is aligned with the empty orbital (LUMO) of the singlet carbene. One of the earlier experimental studies,

that of Yamamoto and Moritani,[30] attempted to determine preferences between the cis and trans olefinic products (eq 8). When both R_a and R_b are alkyl or aryl

$$\tag{8a}$$

cis

$$\tag{8b}$$
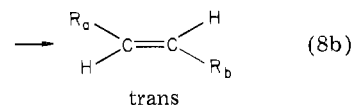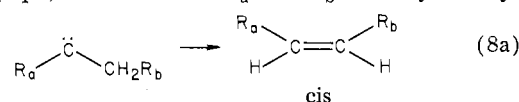
trans

groups, they found trans olefins produced predominantly, while for carboethoxy groups the cis olefin was formed preferentially. Yamamoto and Moritani concluded that both steric and electronic factors influence the stereochemistry.

More recent experimental studies have resulted in a somewhat ambiguous picture concerning the role of electronic considerations. For example, Nickon and co-workers,[36] choosing what appeared to be a relatively rigid, stereochemically well-defined system, reported an exo-H/endo-H migratory ratio of 138. Since the exo hydrogen is in much closer alignment with the empty singlet carbene orbital, such a large migratory ratio supports the theoretical prediction of HZV.[45] Kyba and John[41a] subsequently reported minimal stereoselectivity in the 1,2 H shifts of 4-*tert*-butyl-2,2-dimethylcyclohexylidene, while Press and Shechter[41b] found strong axial stereochemical preferences for migration in the quite similar 4-*tert*-butyl-2-methoxycyclohexylidene. Because of the seemingly inconsistent stereochemical results obtained for different carbenes from experiment, Kyba turned to semiempirical calculations. His MINDO examination[46] of the methylcarbene and unsubstituted cyclohexylidene rearrangements suggests that stereoelectronic control is operative. However, a limited torsional process which places the equatorial H in a position such that it may migrate toward the empty carbene orbital is energetically feasible. However, the very recent experimental results of Shechter[41b] do not appear to support such an interpretation.

A final issue of particular pertinence to the theoretical studies discussed below is the magnitude of activation energies for 1,2 H shifts. To our knowledge there is not a precise experimental activation energy available for any such isomerization. Since these reactions are thought to proceed extremely rapidly, it has often been assumed that 1,2 hydrogen migrations occur with essentially zero activation energies. This result is supported by MINDO calculations of the type developed by Dewar and co-workers.[46,47] However, in 1978 Su and Thornton[43] reported experimental results for the thermal decomposition of 1-phenyl-2-diazopropanes (eq 9). Although a precise activation energy was not reported,

$$\tag{9}$$
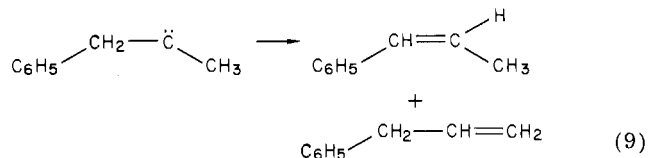
ported, Su and Thornton conclude that "the data presented provide multiple evidence favoring the existence of a barrier to H migration in carbenes".

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Nitrene 1,2 Hydrogen Shifts

In many ways the reactions of nitrenes parallel those of carbenes.[8] However at present nitrenes must be considered a much less completely characterized class of free radicals. In fact, nitrene rearrangements are so rapid that it is often difficult to exclude the possibility that a free nitrene was never present at all.[8,10,11] The general form of the nitrene 1,2 hydrogen shift is

$$R_aR_bHC-\ddot{N}\cdot \rightarrow R_aR_bC=NH \qquad (10)$$
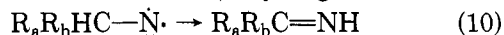
and alkylnitrenes undergo this rearrangement so rapidly that the aziridine addition product

$$R_3C-\ddot{N}\cdot + C_2H_4 \longrightarrow \underset{H_2C-\!\!-\!\!-CH_2}{\overset{\overset{\textstyle CR_3}{|}}{N}} \qquad (11)$$
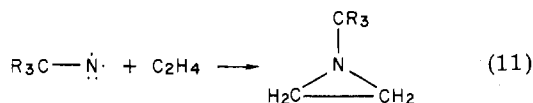
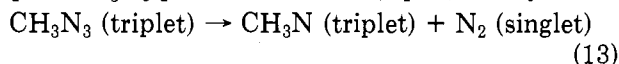has never been observed experimentally.[10,11] This has led experimentalists to the conclusion that the existence of alkylnitrenes as stable minima on potential-energy surfaces is tenuous.[48,49]

The prototype nitrene 1,2 hydrogen shift is the rearrangement of methylnitrene, typically starting from methyl azide (eq 12). Although as noted above the

$$CH_3N-N_2 \longrightarrow N_2 + CH_3-\ddot{N}\cdot \longrightarrow \underset{H}{\overset{H}{>}}C=N\overset{\nearrow H}{} \qquad (12)$$
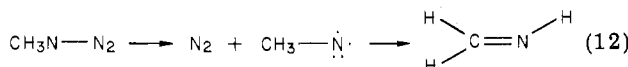
existence of methylnitrene has never been definitely established experimentally, it appears to be the major primary product in the photolysis of methyl azide in the gas phase or in low-temperature matrices.[48,50-53] Milligan's infrared matrix isolation study[51] was apparently the first to establish the methylenimine product of (12), thus indirectly confirming the importance of methylnitrene formation.

Since the theoretical section of this Account does not analyze the methylnitrene hydrogen migration (eq 12), a few comments are appropriate here. Although the rapid rearrangement of singlet CH_3N is supported by theory,[54,55] the $^3A_2$ ground state should be very long-lived in the absence of collisions, and hence observable by ESR spectroscopy.[56] This is true because the triplet ground state of CH_3N lies below the lowest triplet state of methylenimine, thus making the triplet 1,2 hydrogen shift extremely unlikely under normal conditions. If as suggested[48,52] the methyl azide dissociation energy $D(CH_3N-N_2)$ is only $\sim$40 kcal, then at threshold there may not be enough energy available to any triplet CH_3N product to allow the 1,2 hydrogen shift. Note, of course, that such a photodissociation process must occur on a triplet CH_3N_3 potential surface (eq 13). Any disso-

$$CH_3N_3 \text{ (triplet)} \rightarrow CH_3N \text{ (triplet)} + N_2 \text{ (singlet)} \qquad (13)$$

ciation (to yield $^3A_2$ CH_3N) on a singlet potential surface would require the much greater energy needed to produce triplet molecular nitrogen $[\Delta E(X\,^1\Sigma_g^+ - A\,^3\Sigma_u^+) = 142 \text{ kcal}^{57}]$.

Vinylidene 1,2 Hydrogen Shifts

Here we will consider a vinylidene to be a molecular entity of the general form

$$\underset{R_a}{\overset{R_b}{>}}C=C:$$

Such species were referred to as methylenecarbenes by Hartzler in his 1975 review[58] and as alkylidenecarbenes by Stang in his recent review[9] and are members of the larger class of unsaturated carbenes. For the hydrogen migration reaction to occur, one of the groups R_a or R_b must be a hydrogen atom (eq 14). Vinylidenes have

$$\underset{R_a}{\overset{H}{>}}C=C: \longrightarrow R_a-C\equiv C-H \qquad (14)$$
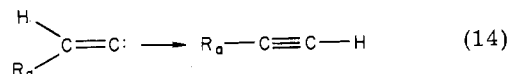
an even shorter history[9,58-61] than nitrenes, but recent experimental developments, especially the vinyl triflate chemistry of Stang,[59] suggest a rich future for the field. The relevance of these species to the present Account is the fact that the rearrangement (eq 14) to acetylenes is probably the single reaction most characteristic of hydrogen-containing vinylidenes.

The prototype rearrangement for vinylidenes is the primitive (i.e., $R_a = R_b = H$) vinylidene reaction

$$\underset{H}{\overset{H}{>}}C=C: \longrightarrow H-C\equiv C-H \qquad (15)$$
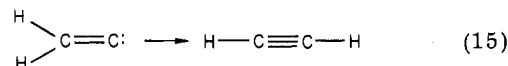
Since no unsaturated carbene has to date been observed spectroscopically, it is no surprise that few detailed experimental studies of $H_2C=C$: have been completed. In fact the only evidence for the (transient) existence of the primitive vinylidene comes from the research of Skell and co-workers.[62-64] Skell and Plonka[62] found that the highly reactive diatomic C_2 abstracts two hydrogens from acetone to yield vinylidene, which then rearranges to acetylene via (15). In a second paper Skell, Fagone, and Klabunde[63] observed the same migration (eq 15) upon reacting C_2 with propane, but in that system the $H_2C=C$: primarily reacts intermolecularly. The presence of primitive vinylidene as a discrete species (minimum on the C_2H_2 potential surface) is not established from the Skell experiments. However, the intermediacy of $H_2C=C$: in the reaction of C_2 with hydrogen-containing compounds to yield acetylene seems incontestable.[64]

As discussed above for the analogous nitrenes, considerable research has been directed toward the issue of whether a discrete vinylidene species is implicated in reactions leading to acetylenes.[9] For example, as far back as 1955 phenylvinylidene was suggested[65] as an intermediate in the formation of phenylacetylene from β-styryl bromide and C_6H_5Li (eq 16). However, careful

$$C_6H_5CH=C: \rightarrow C_6H_5-C\equiv C-H \qquad (16)$$

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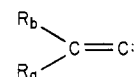(53) E. Koch, *Tetrahedron*, **23**, 1747 (1967).
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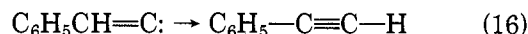(55) J. Demuynck, Y. Yamaguchi, and H. F. Schaefer, unpublished.
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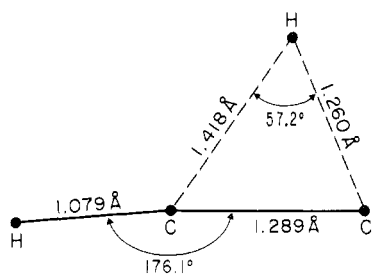
Figure 1. Transition-state structure for the vinylidene–acetylene isomerization occurring on the lowest singlet ($S = 0$) potential-energy surface.

stereochemical studies by Schlosser and Ladenberger[66] on closely related systems have ruled out this possibility. Nevertheless the same 1,2 hydrogen shift (eq 16) appears to be a plausible intermediate in the thermal scrambling of phenylacetylene at elevated temperatures.[67]

Theoretical Studies of the 1,2 Hydrogen Shift

Given the impressive body of experimental research on hydrogen migration reactions in carbenes, nitrenes, and vinylidenes, the casual reader might be tempted to ask whether there is a real need for theoretical examination of these reactions. For several reasons the answer to this question must be in the affirmative. First, many of the simplest (or most fundamental, depending on one's perspective) carbenes, nitrenes, and vinylidenes are difficult to study experimentally. For example, we noted in the previous sections that it is unclear from experiment whether either methylnitrene or vinylidene exist as discrete chemical species. Several other short-lived radicals which have thus far eluded experimental characterization are discussed in the following sections of this Account. Moreover, it is becoming increasingly clear that for the simplest reactions theory is now able to provide a level of mechanistic clarity which is not possible based on strictly experimental findings. For example, it is now possible[68] (for reactions involving as many as six atoms) to predict the structures of transition states to within a few hundreds of an angstrom.

The Singlet and Triplet Vinylidene–Acetylene Rearrangements. The very simplest diradical 1,2 hydrogen shift is shown in reaction 15. During the past 2 years we have completed reliable theoretical studies of both the lowest singlet[69] and triplet[70] potential-energy surfaces for the vinylidene → acetylene reaction. Although it was not assumed that this reaction shares the characteristics of the carbene and nitrene rearrangements, we will in hindsight note at least two striking similarities between (15) and the methylcarbene → ethylene reaction (eq 3).

The first level of theory at which the singlet H_2CC: rearrangement was examined employed a double ζ (DZ)

basis set and single configuration self-consistent-field (SCF) procedures. This approach utilizes two basis functions for each atomic orbital of the constituent atoms and yields hydrocarbon equilibrium geometries in very good agreement with experiment.[71]

The singlet transition state found in this manner is illustrated in Figure 1. Since this simple isomerization is exothermic by ~40 kcal, Hammond's postulate[72] would suggest that the transition state should closely resemble the reactants. However Figure 1 shows clearly that the transition state is structurally intermediate between reactant vinylidene and product acetylene.

Since Skell and co-workers[62–64] were (on the basis of their experiments on this reaction) skeptical concerning the existence of vinylidene as a discrete intermediate, the predicted barrier of 26 kcal is quite surprising. However, when electron correlation is variationally accounted for by the method of self-consistent electron pairs (SCEP),[73] the barrier is reduced to 18 kcal. Even more important, when polarization functions (d functions on carbon, p functions on hydrogen) are added to the basis set, the SCEP barrier is reduced to 8 kcal.[74] Although estimates of further theoretical corrections are difficult, we suggest that the true barrier is not less than 5 kcal, a prediction consistent with the short lifetime[64] of singlet H_2CC:. To observe vinylidene spectroscopically, it is apparent that it must be prepared with a very small amount (perhaps 5 kcal) of internal energy. Otherwise the 1,2 hydrogen shift to acetylene will take place straightaway.

The generality of this prediction is suggested by the DZ SCF prediction of Csizmadia[75] that the barrier height for the methylcarbene → ethylene reaction (eq 3) is 27 kcal. There is every reason to expect that the neglect of polarization basis functions and correlation effects for (3) will lead to errors qualitatively similar to those found for (15). Thus we suggest a barrier of 5–8 kcal for the methylcarbene rearrangement. This prediction is entirely consistent with Thornton's experimental finding[43] of nonzero barriers for carbene 1,2 hydrogen shifts. However even a small barrier of this size differs from Dewar's MINDO/2 prediction[47] of no barrier at all for (3).

As might be expected from the experimental work of Sohn and Jones,[32] the triplet vinylidene → acetylene reaction has a larger barrier. However the magnitude of this barrier is no less than 55 kcal,[70] after the effects of polarization functions and electron correlation have been properly treated theoretically. Again we can make the connection with methylcarbene by citing Csizmadia's DZ SCF prediction[76] of 88 kcal for the triplet isomerization (3). Since we find the analogous DZ SCF procedure to yield a 72-kcal barrier for the vinylidene isomerization, it is apparent that triplet methylcarbene faces a large activation energy to rearrangement. Similarly, as noted above, we expect other triplet nitrenes, vinylidenes, and carbenes to be very stable

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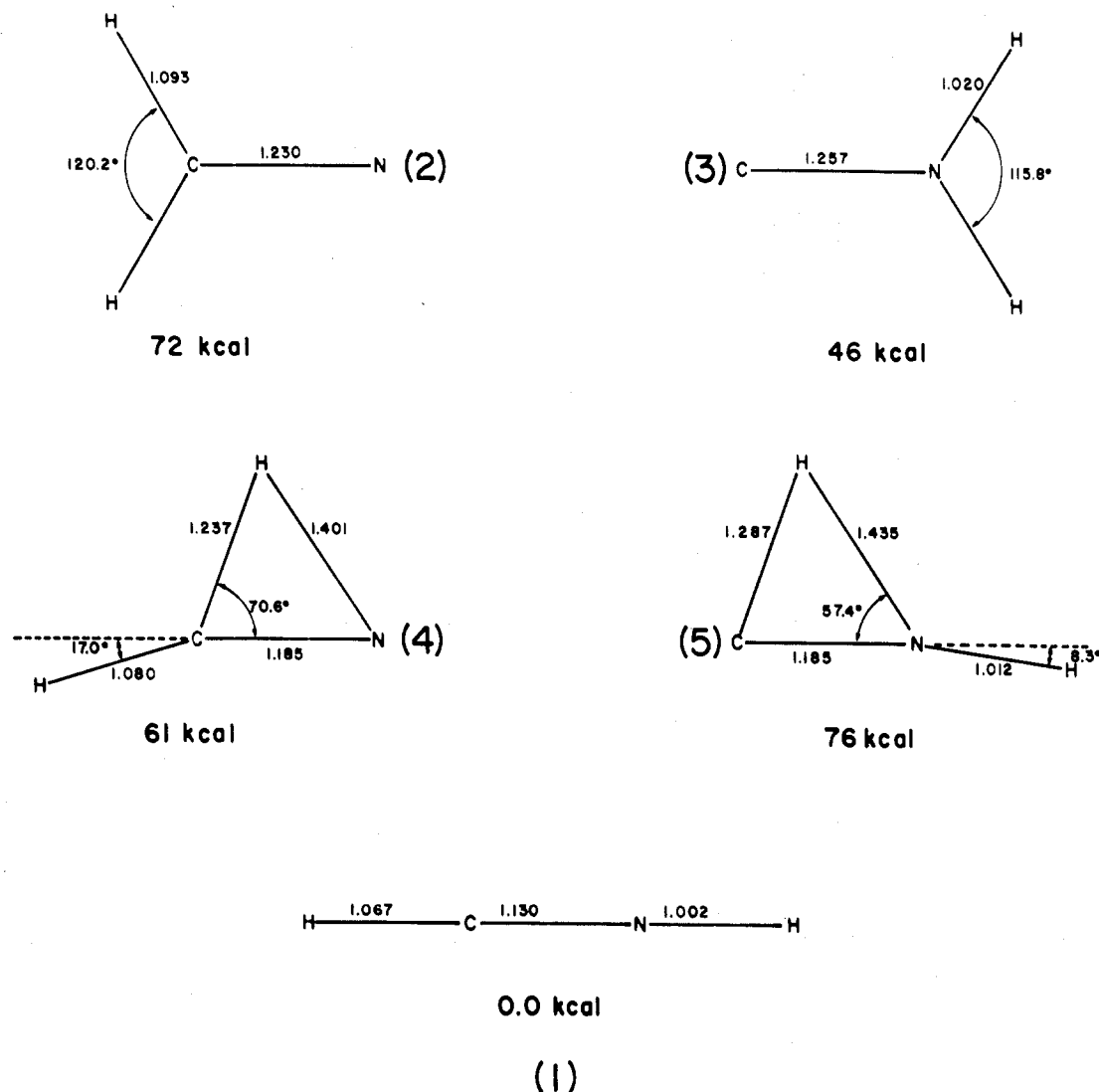
Figure 2. Predicted structures and relative energies in kcal/mol for three isomers of H_2CN^+ and the transition states connecting them. Bond distances are in Å.

with respect to isomerization, in the absence of collisions. Probably the most striking mechanistic feature of the triplet isomerization is its nonplanar transition state.[70] However, such a transition state is consistent with the fact that the lowest excited state of acetylene is the cis $^3B_2$ state.[77]

Some Interstellar Isomerizations. The H_2CN^+ molecular ion is generally agreed[78] to play a critical role in the formation of interstellar HCN and HNC. The obvious problem that H_2CN^+ has not yet been identified in interstellar space is complicated by considerable uncertainty due to the existence of three distinct isomers of H_2CN^+, labeled (1), (2), and (3) in Figure 2. The easiest connection between these three isomers is via two different 1,2 hydrogen shifts, for which transition states are illustrated in Figure 2.

In a recent communication Brown[79] stated that although the isomer (3) with two hydrogens bonded to nitrogen had been completely neglected in previous discussions, it is likely to have a crucial role in the formation of HNC. This logic follows from the fact that

the fast ion–molecule reaction generally thought responsible for HCN formation is

$$C^+ + NH_3 \rightarrow H_2CN^+ + H \qquad (17)$$
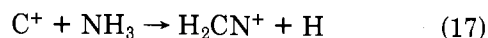
followed by dissociative recombination

$$H_2CN^+ + e^- \rightarrow (HNC, HCN) + H \qquad (18)$$

Brown argued that reaction 17 should lead exclusively to isomer (3), since formation of the more stable linear isomer (1) would require an energetically costly 1,2 hydrogen shift from nitrogen to carbon.

A theoretical study by Conrad and myself[80] was designed to test Brown's hypothesis. Using DZ + P configuration interaction methods similar to those described above for the vinylidene → acetylene system, the relative energies given in Figure 3 were predicted. Our first surprise was that the isomer (3) with both hydrogens bonded to nitrogen lies much lower in energy than that with the H atoms bound to carbon. This result is obviously contrary to chemical intuition based on the fact that H_2CO rather than H_2OC is the energetic minimum for formaldehyde.

Perhaps even more surprising is the fact that isomer (2) is not even a relative minimum on the H_2CN^+

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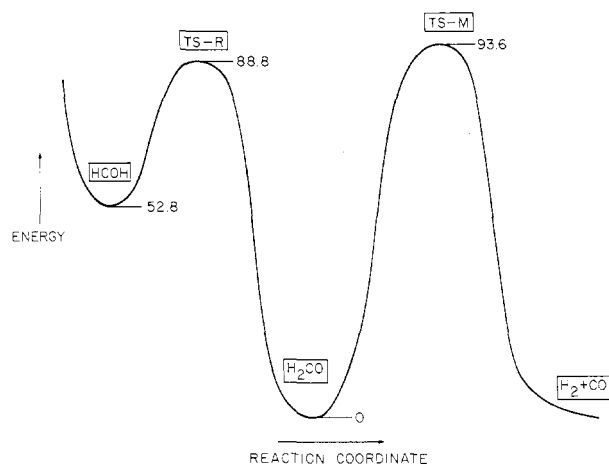
Figure 3. Qualitative view of the lowest singlet potential-energy surface for H_2CO, the isomer HCOH, and the products H_2 + CO. See text for the effects of zero-point energies on the predicted barrier heights.

potential surface. Actually, however, this is reminiscent of the role experimentalists have suggested[48] that alkylnitrenes play in the photolysis of azides to eventually yield imines. In any case, Brown's isomer (3) does correspond to a potential minimum and faces a large barrier ($\sim$30 kcal) to its obvious 1,2 hydrogen shift. Our mechanistic conclusion about these two singlet isomerizations is that they are *very* different from the isoelectronic vinylidene isomerization. It seems clear that the 1,2 hydrogen shifts of molecular ions cannot be readily understood in terms of the reasonably consistent picture derived from free-radical rearrangements.

Unfortunately Brown's otherwise superb logic[79] was marred by the fact that reaction 17 is highly exothermic, by $\sim$143 kcal. Thus we were forced to conclude[80] that while reaction 17 does initially form Brown's isomer (3), even under interstellar conditions, isomer (3) is formed with 67 kcal of internal energy. This is more than enough to surmount the hydrogen migration barrier of 30 kcal, and thus nearly all H_2CN^+ ions end up in the linear isomer (1). The simplest picture then suggests that HCN and HNC should be formed in comparable amounts via the exothermic dissociative recombination (eq 18). This prediction is in rough agreement with interstellar observations.

Role of Hydroxycarbene in Formaldehyde Photochemistry. In a recent communication,[81] we noted the fact from organometallic studies of metal–carbene complexes that when an alkoxycarbene ligand is split off from the metal, a hydrogen migration occurs almost immediately to yield an aldehyde product.[82] This suggests a reasonably low activation energy, which might also apply to the simplest such rearrangement

$$\overset{HO}{\underset{H}{\diagdown}} C: \longrightarrow \overset{O}{\underset{H}{\overset{\|}{\diagdown}} C} \diagdown H \qquad (19)$$
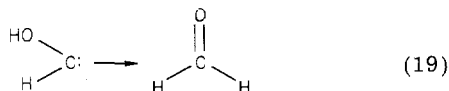
A low barrier for the hydroxycarbene–formaldehyde isomerization might in turn help unravel the mechanistically foreboding photodissociation of formaldehyde (eq 20). Since (20) takes place much more slowly than

$$H_2CO(S_0) \xrightarrow{h\nu} H_2CO(S_1) \rightarrow I \rightarrow H_2 + CO \quad (20)$$
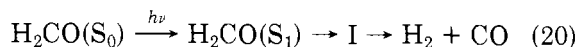
intuitively expected, Houston and Moore[83] suggested the presence of an intermediate state (I) and even went so far as to suggest HCOH as one possibility.

This first reliable theoretical examination[81] of HCOH, hydroxycarbene, clearly established that the trans singlet lies only about 52 kcal above ground-state S_0 formaldehyde. Thus HCOH lies well below the 80.6 H_2CO S_1 origin, and the only remaining question concerns the barrier height for (19). John Goddard has now completed a detailed study[84] (DZ + P basis set, large CI) of the HCOH $\rightarrow$ H_2CO transition state and finds it 88.8 kcal above H_2CO. Corrections for zero-point energies yield a predicted activation energy of 89.3 kcal. Considering that the molecular transition state for $H_2CO \rightarrow H_2$ + CO lies at 93.6 kcal, it is clear that HCOH could play a role (see Figure 3) in formaldehyde photochemistry. However, the molecular transition state has 6.6 kcal less zero-point energy than formaldehyde itself, reducing the predicted activation energy to 87.0 kcal.

The explanation of why products are seen at formaldehyde energies (e.g., 81 kcal) lower than 87 kcal (the predicted activation energy) is quite surprising. Miller[85] has very recently shown that at energies near 81 kcal, the rate of quantum mechanical tunneling through a zero-point corrected barrier of 87 kcal *is* large enough to explain the experimental observations. Although HCOH may be formed from S_1 H_2CO radiationless transitions, it rather quickly tunnels back to H_2CO, and there is no reasonably low barrier for HCOH $\rightarrow$ H_2 + CO. Thus our current thinking is that while HCOH may be frequently "visited" in the course of H_2CO photodissociation, it does not play an important mechanistic role. We have established that HCOH is a stable molecular entity, and one indirect experimental observation has within the past few months been reported.[86]

At the present time we do not have an entirely satisfactory qualitative explanation why hydroxycarbene (unlike most carbenes, nitrenes, and vinylidenes) has a sizeable activation energy ($\sim$35 kcal) for the singlet 1,2 hydrogen shift to formaldehyde. However the isoelectronic aminonitrene $\rightarrow$ diimide singlet barrier is also high, making it apparent that the HCOH barrier is by no means unique.

Silaethylene, Methylsilylene, and Silylmethylene. Although a great deal of experimental research[87] has been directed toward the synthesis of H_2SiCH_2, it has been appreciated less often that two other isomers are connected to silaethylene via 1,2 hydrogen shifts (eq 21). In a recent theoretical paper Gordon[88] drew at-

$$H_3Si{-}\overset{..}{C}\diagdown_H \longrightarrow H_2Si{=\!=}CH_2 \longrightarrow H{-}\overset{..}{Si}\diagdown_{CH_3} \quad (21)$$
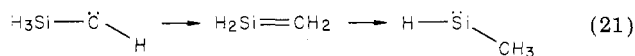
tention to this inequity and made a number of minimum basis set calculations. Quite surprisingly, Gordon

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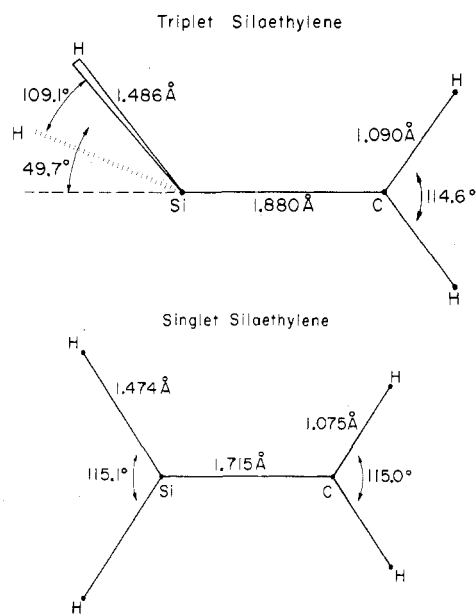(88) M. S. Gordon, *Chem. Phys. Lett.*, **54**, 9 (1978).

Figure 4. Predicted equilibrium geometries for triplet and singlet silaethylene. For the former, the rocking angle 49.7° is defined as the angle between the C–Si axis and the HSiH plane.

predicted the lowest singlet isomer to be methylsilylene, lying ~7 kcal below silaethylene. In contrast silyl-carbene is predicted to be quite high lying, 55 kcal above CH_3SiH. Strausz and co-workers[89] recently reported a similar ordering of $CSiH_4$ states.

A dramatic example of the failure of simple ab initio methods is seen for silaethylene itself. For the singlet–triplet separation, minimum basis SCF methods predict $\Delta E = -1.4$ kcal, i.e., the triplet state is predicted to lie lower. At the DZ SCF level, ΔE is increased to a plausible value, $\Delta E = 13.7$ kcal. However recent studies by Hood[90] employing d functions on C and Si and treating electron correlation in a rather complete manner (4097 $^1A_1$ configurations and 9759 $^3A''$ configurations) yielded the first reliable singlet–triplet separation, 38.5 kcal. Comparison of the three separations −1.4, 13.7, and 38.5 kcal shows that overly simplistic theoretical models can yield very unrealistic theoretical predictions. The predicted structures of singlet and triplet silaethylene are seen in Figure 4.

John Goddard[91] has just completed a definitive theoretical characterization of the structures and relative energies of the three singlet $CSiH_4$ isomers. At the DZ SCF level the relative energies of H_3SiCH, H_2SiCH_2, and $HSiCH_3$ are 63.5, 0.0, and −11.5 kcal, respectively. With this double ζ basis set, configuration interaction (CI) including single and double excitations yields for the same three relative energies 76.4, 0.0, and −2.3 kcal. CI using a more complete DZ + d basis set provides our final prediction, that methylsilylene lies only 0.08 kcal below silaethylene, while silylmethylene lies 69.4 kcal above silaethylene. The near degeneracy of H_2SiCH_2 and $HSiCH_3$ is especially intriguing, and we intend to investigate the singlet potential surface connecting these two fascinating species.

Metal–Vinylidene Systems. This Account's final subject for theoretical discussion was brought to our
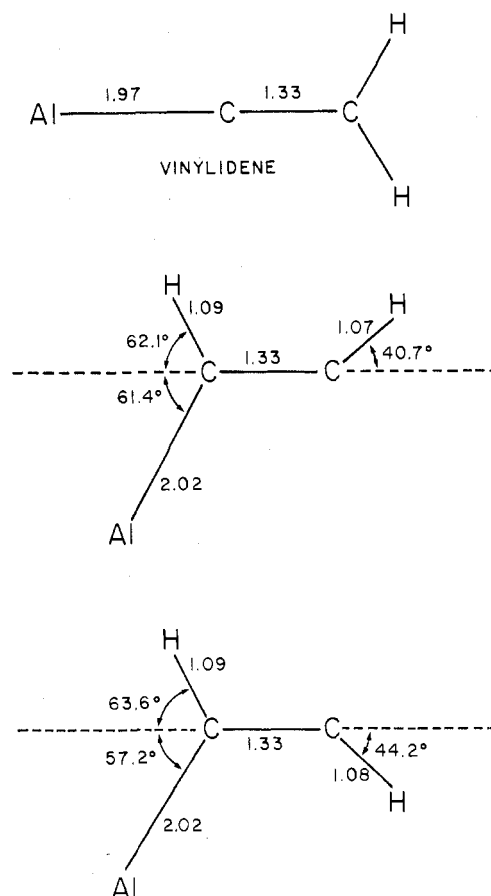

Figure 5. Predicted equilibrium geometries for the vinylidene and σ-bonded isomers of $Al-C_2H_2$. There are two conformers of the σ-bonded system, with the terminal hydrogen lying trans (the middle structure) or cis (the lowest structure) to the Al atom. Bond distances are in Å.

attention by two recent experimental communications by Kasai and McLeod. They reported the syntheses of the aluminum atom–ethylene and aluminum atom–acetylene[92] adducts. From the electron spin resonance (ESR) spectra of these new molecules, Kasai and McLeod drew some qualitative conclusions concerning their molecular structures. Although the ESR data suggest a conventional π-bonded structure for $Al-C_2H_4$, Kasai and McLeod suggest a very different sort of equilibrium geometry for $Al-C_2H_2$. In the latter case, an Al–C σ bond seems more consistent with the experimental data, and the resulting structure is quite reminiscent of the vinyl radical.

Since we had previously shown[93] the $Mn=C=CH_2$ vinylidene complex to be energetically comparable to the analogous π-bonded acetylene structure, it immediately occurred to us to examine the $Al=C=CH_2$ structure. From this perspective the equilibrium geometries seen in Figure 5 were obtained. Large-scale CI techniques were then used to predict reliable energies for the different isomers.[94]

Consistent with the experimental conclusions of Kasai and McLeod,[92] we predicted the σ-bonded or vinyl radical like structure to lie energetically below the π complex. Actually there are two conformers of the

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vinyl structure, lying only 0.15 kcal apart, with the cis being the lower lying, bound by $\sim$8 kcal relative to separated Al + C_2H_2. However the vinylidene structure lies 12 kcal lower and is the absolute minimum on the AlC_2H_2 potential-energy surface.

Since the vinylidene structure is inconsistent with Kasai, McLeod, and Watanabe's ESR spectrum, there may appear to be a conflict between theory and experiment. However, the barrier height between vinylidene and acetylene is 5–8 kcal and might not be greatly altered by the presence of the Al atom. If this is the case, then the 1,2 hydrogen shift (eq 22) might not occur at all at the liquid helium temperatures of Kasai and McLeod.[92]

$$\text{(22)}$$
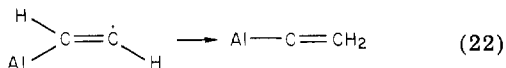
The most challenging feature of Trenary's study[94] is that while the isolated acetylene–vinylidene reaction is *endothermic* by 40 kcal, the same process becomes *exothermic* in the presence of an Al atom. We suspect that other endothermic reactions such as the methylcarbene–ethylene and methylnitrene–methylenimine

rearrangements will also become favorable when complexation to a metal atom, metal cluster, or metal surface is achieved. This general mechanism for using metal systems to transform endothermic reactions into nearly degenerate rearrangements may play a key role in catalysis and surface chemistry.

Concluding Remarks

It should be clear that the 1,2 hydrogen shift is a remarkably ubiquitous and important chemical reaction. This simple rearrangement plays a key role in physical organic chemistry, in the chemistry of interstellar space, and in the rapidly developing organometallic-surface-catalysis branch of chemistry. Further studies, both experimental and theoretical, can be expected to yield many new insights during the 1980's.

Optical Activity in Vibrational Transitions: Vibrational Circular Dichroism and Raman Optical Activity

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Received November 14, 1978

Natural optical activity in vibrational transitions is emerging as a new branch of molecular spectroscopy. Two distinct yet complementary physical phenomena are the focus of this new field, known as vibrational optical activity (VOA). The first of these is the difference in absorbance of left vs. right circularly polarized infrared radiation, referred to as vibrational circular dichroism (VCD), and the second is the difference in scattered intensity of left vs. right circularly polarized incident laser radiation, which is termed Raman optical activity (ROA). Both theoretically and experimentally, VOA is at an early stage of development. Work is currently in progress to increase the range and efficiency of measurement techniques, to uncover empirical and simple theoretical trends in experimental data, to develop theoretically sound models for calculation, and to compare theoretical and experimental results.

Vibrational optical activity is the convergence of the two established fields of electronic optical activity

(EOA) and vibrational spectroscopy. Considered separately, these two fields already provide powerful techniques for obtaining structural information from molecules. The combination of these two fields is expected to generate a number of significant advantages. From the viewpoint of vibrational spectroscopy, VOA should provide configurational and enhanced conformational sensitivity to methods that are already highly structure sensitive. From the viewpoint of optical activity, one can regard the vibrational region as consisting of an abundance of chromophores representing virtually all portions of the molecule. Thus, VOA should provide new chromophores and new sets of criteria for the determination of absolute configuration in molecules. In addition, VOA should also be very sensitive to the conformation of molecules in solution. In fact, the combination of complete VCD and ROA spectra may contain enough stereochemical information to completely determine the conformation of the molecule under study.

The primary difficulty in the measurement of VOA is that signals are four to five orders of magnitude smaller than the parent effects, infrared absorption and Raman scattering. As a result, both VCD[1,2] and ROA[3,4]

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