Registry No. Diazofluorene, 832-80-4; fluorenylidene, 2762-16-5; *trans*-1,2-dichloroethylene, 156-60-5; *cis*-1,2-dichloroethylene, 156-59-2; 9-(2,2-dichloroethylene)fluorene, 87319-65-1; styrene, 100-42-5; 1,3-butadiene, 106-99-0; hexafluorobenzene, 392-56-3; 1,1,2-trichlorotrifluoroethane, 76-13-1; perfluoromethylcyclohexane, 355-02-2; tetramethylsilane, 75-76-3; benzene, 71-43-2; methanol, 57-56-1; 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine, 26939-18-4; fluorenone, 486-25-9; 2-((9-hydroxyfluorenyl)methyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine, 88687-13-2; 2-((9-hydroxyfluorenyl)methyl)-4,4,6-trimethyl-2,3,5,6-tetrahydro-1,3-oxazine, 88687-14-3; fluorenylidenacetaldehyde, 4425-71-2; *trans*-2,3-dichlorospiro[cyclopropane-1,9′-fluorene], 87319-64-0; *cis*-2,3-dichlorspiro[cyclopropane-1,9′-fluorene], 87319-63-9; 2-phenylspiro[cyclopropane-1,9′-fluorene], 10423-18-4; 2-vinylspiro[cyclopropane-1,9′-fluorene], 57393-06-3.

Thermal and Photochemical Deazetations of Fluorine-Substituted 4-Methylenepyrazolines. The Kinetic Behavior of Trimethylenemethanes

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Abstract: 4-(Difluoromethylene)-1-pyrazoline and 4-(fluoromethylene)-1-pyrazoline were observed to undergo thermal and photochemical deazetation in the gas phase as well as in solution to form mixtures of methylenecyclopropanes. The gas-phase and solution-phase, thermal, and photochemical results are contrasted, and the observed kinetically controlled product ratios are compared with the very different equilibrium values. As a result, mechanisms involving trimethylenemethane diradicals are proposed for both processes. The photochemical reactions seem to be dominated by "hot" reactions of vibrationally excited TMM's, while the thermal reactions show interesting selectivity in their cyclization processes.

A recent study of the thermal equilibration of difluoromethylenecyclopropanes **1** and **2** demonstrated a moderate thermodynamic preference of vinylic, substitution over cyclopropyl substitution for geminal fluorine substituents.[1] In short, a substantial geminal destabilization of the fluorine substituents on **1**, coupled with a slight inherent preference of allylic over vinylic geminal fluorine substitution, leads to the observed excess of **2** at equilibrium.[2–5]

1 2

$\Delta H° = -1.9$ kcal/mol
$\Delta S° = -0.5$ eu

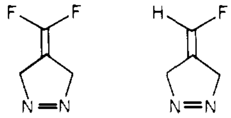
While the mechanism for the above rearrangement is generally conceded to involve trimethylenemethane (TMM) diradicals, neither the thermodynamic nor the accompanying kinetic data give *any* insight into the structure or the kinetic fate of such diradicals. Moreover, while "orthogonal" TMM's have been logically, and most likely correctly, implicated in a number of such rearrangements[6] and "planar" TMM's have been demonstrated to be "kinetically accessible" in others,[7,8] there is still no direct *experimental* evidence for the ground-state structure of singlet TMM's which have no steric impediment to planarity.

Table I. Product Ratios for Thermolysis and Photolysis of 4-(Difluoromethylene)-1-pyrazoline (3)

conditions	1	2	allene
162 °C, 5 mm, 15 min[a]	54.2	45.8	
162 °C, 700 mm, 15 min[b]	54.4	45.6	
150 °C, soln, 30 min	59.7	40.3	
$h\nu$, 2 mm, 30 min[c]	30.1	31.6	38.3
$h\nu$, 660 mm, 30 min[b]	56.6	42.2	1.2
$h\nu$, soln, 60 min	61.6	38.4	
equilibrium values, 193 °C[d]	14.2	85.8	

[a] Good first-order kinetics observed. [b] Argon added. [c] All photolyses at 38 °C and 3500 Å. [d] Reference 1.

It was our expectation that *some* significant insight into the nature of such TMM's might be gained by examining the *kinetic* behavior of those fluorine-substituted TMM's which could be generated by thermal or photochemical deazetation of pyrazolines **3** and **4**, which could be synthesized by diazomethane cycloaddition to 1,1-difluoroallene and fluoroallene, respectively.[9]



3 4

While there is not universal agreement on the mechanism for deazetation of such pyrazolines,[6,10] it is generally accepted that *photochemical* deazetation does produce a trimethylenemethane species. The most direct evidence for this is the spectroscopic

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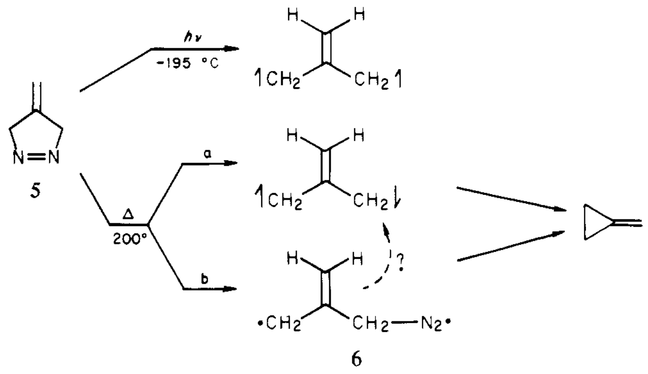
Table II. Product Ratios for Thermolysis and Photolysis of 4-(Fluoromethylene)-1-pyrazoline (4)

conditions	9	10
168 °C, 1 mm, 15 min[a,b]	81.7	18.3
168 °C, 740 mm, 10 min[c]	86.8	13.2
140 °C, CCl_4, 30 min	90.5	9.5
$h\nu$, 2 mm, 30 min[d]	48.0	52.0
$h\nu$, 657 mm, 30 min[c]	49.8	50.2
$h\nu$, CCl_4, 60 min	64.6	35.4
equilibrium values, 229 °C[e]	11.5	88.5

[a] Good first-order kinetics observed. [b] No time dependence noted for product ratios. [c] Argon added. [d] All photolyses at 38 °C and 3500 Å. [e] Reference 15.

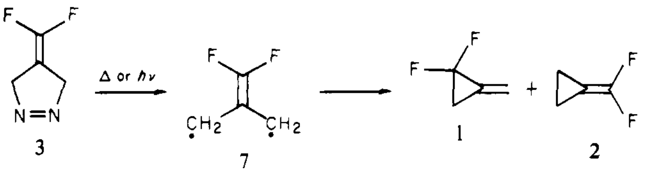
observation of the parent triplet trimethylenemethane via photochemical deazetation of 4-methylene-1-pyrazoline (**5**) in a matrix.[11,12] As for the *thermal* conversion of **5** to methylenecyclopropane, the intermediacy of a trimethylenemethane intermediate (here necessarily a singlet) is open to question, with a great deal of indirect evidence having recently been accumulated by Crawford in favor of a diazenyl allyl diradical species (**6**) being the *product-forming* intermediate.[13,14]



While the invokation of **6** to the exclusion of trimethylenemethane involvement is as we will see not a "uniquely required" conclusion, it was expected that a thorough thermal and photochemical, gas-phase and solution-phase study of the deazetations of **3** and **4** would shed considerable light on such mechanistic questions.

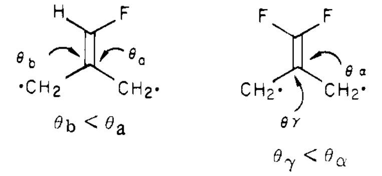
Results and Discussion

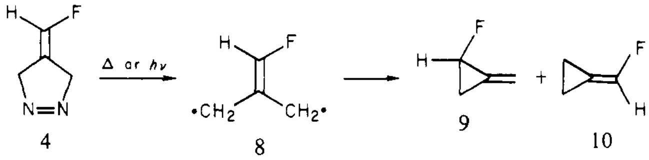
Nitrogen extrusion from 4-(difluoromethylene)-1-pyrazoline (**3**) was studied both thermally and photochemically in the gas phase at various pressures and in CCl_4 solution. The results of these studies are reported in Table I. The lack of time dependence on the product ratios indicates that the product ratios are true *kinetic* ratios, with the products stable to the thermolysis and photolysis conditions.



Deazetation of 4-(fluoromethylene)-1-pyrazoline (**4**) was similarly studied with the results shown in Table II. The reported equilibrium results for **9** ⇄ **10**[15] are consistent with earlier observations that indicate a single fluorine substituent to give rise to no unusual thermodynamic effects.[2,3] The observed ratio of **9**:**10** is consistent with a general thermodynamic preference of *all* single substituents for vinylic over allylic positions.

Chart I





In our initial discussion we will presume to invoke the commonality of TMM diradicals as the product-forming intermediates for both the thermal and the photochemical deazetations of **3** and **4**. While the question of concerted vs. stepwise deazetation cannot be addressed by these studies, the discussion on the possible involvement of diazenyl allyl diradicals as the *product-forming intermediates* will be deferred until later.

A comparison of the observed product ratios for deazetation of **3** and **4** with the equilibrium ratios clearly indicates that relative thermodynamic stability of products is *not* a dominant factor in product determination for these processes. From the pressure effect on the product ratios, it is obvious that the photochemical deazetations, not unexpectedly, led to "hot", that is vibrationally excited, intermediates. In the case of the photolysis of **3**, this gave rise to a significant amount of CF_2: extrusion to form allene ($E_a \approx 56$ kcal/mol)[16] at very low pressures. It appears that the allene was formed largely at the expense of **1**, as is to be expected on the basis of our knowledge of the thermal CF_2: extrusion processes of *gem*-difluorocyclopropanes.[17] A second hot process, that of equilibration of **1** and **2** and of **9** and **10** ($E_a \approx 38$ kcal/mol),[1] was also observed to be significant at low pressures, with the higher E_a extrusion process, as expected, being cooled more effectively than the isomerization process as the pressure was increased. Nevertheless, it is expected that both of these "hot" processes would have been effectively cooled by the time solution conditions were reached. While there is evidence for hot reactions in solution,[18] such processes should only be expected for *very* low activation energy reactions.

Such a very low activation energy process, which most probably is *not* quenched in solution, is that of *cyclization* of the proposed TMM intermediates **7** and **8** ($E_a < 10$ kcal/mol)[19] derived from the deazetations of **3** and **4**. The effect of such hot processes would be to *level* the differences of the two competitive rate process toward the statistical value of 67:33 in each case. If one were to assume that, even in solution the photochemical deazetations of both **3** and **4**, TMM intermediates **7** and **8** cyclize to products virtually exclusively via *hot* processes, one would expect results similar to those observed, i.e., ratios of 61.6:38.2 and 64.6:35.4 for cyclizations of **7** and **8**, respectively.

When the activation energy of cyclization is no longer a factor, as we expect in the photochemical deazetations, activation *entropy* factors may become dominant. The observed slight deviations from 2:1 ratios in each case could derive from subtle entropy factors. Deviations from the perfect symmetry of parent (C_4H_6) TMM by TMM's **7** and **8**, as depicted in Chart I, might be predicted on the basis of the calculated structures of 1-fluoro-

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propenes[20] and could give rise to small entropy-derived differences in cyclization rate.

Thermal Deazetation

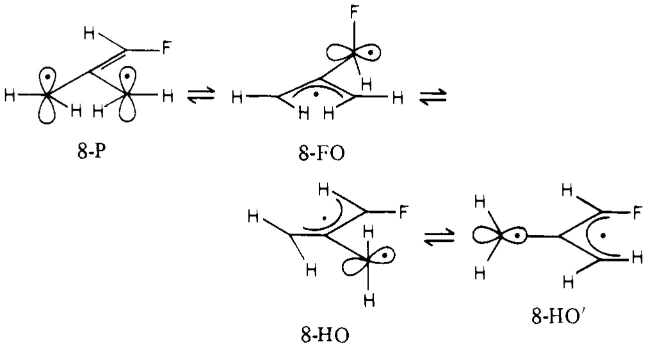
The thermal processes are another matter completely. The improbability of hot processes being implicated in the cyclizations of **7** or **8** is strongly implied by the significant kinetic preference for cyclization to **9** shown in the deazetation of **4**. This preference can be easily rationalized on the basis of *either* a TMM conformational preference of orthogonal CHF (thus leading to preferred involvement of CHF in cyclization) *or* a significantly (~ fivefold) rate preference for rotation (cyclization) of the CHF terminus. Either circumstance can be rationalized as reasonable. While *geminal* fluorine substituents demonstrate unusual behavior and seem to stabilize neither alkene nor radical sites to a significant extent,[3,21,22] a *single* fluorine substituent appears to behave in a normal manner[3] and thus *stabilizes* an alkene site and in all probability stabilizes a radical site even more substantially than other halogens as it has been shown to do for cationic sites.[23]

Thus, cyclization of TMM **8** could well give rise to a significant preference for CHF incorporation into the ring and result in the 90:10 limiting ratio for **9**:**10** in solution.

In contrast, cyclization of TMM **7** shows little deviation from statistical product formation with CH_2 incorporation apparently being slightly preferred under limiting kinetic-controlled conditions. Such a small preference could be derived either from small E_a or $\Delta S^‡$ differences.

General Discussion

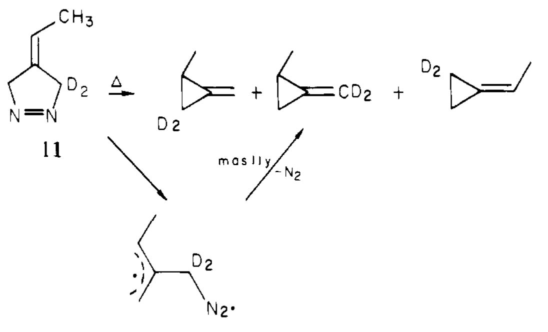
It should be understood that the kinetic analyses given above derive from an implicit oversimplification of the TMM systems involved. As exemplified for TMM **8**, such TMM's are actually



equilibrating mixtures of conformers. Undoubtedly, in the photochemical deazetation, **7** and **8** are rapidly equilibrated by yet another unquenchable "hot" process, prior to cyclization, a process which undoubtedly contributes to the "random" nature of the product distributions in both systems.

Likely in the case of the thermal deazetation, the conformational equilibration is incomplete and perhaps even unfavorably competitive with cyclization.

It is this likelihood that allows the proposed TMM intermediacy mechanism to remain consistent with the interesting stereochemical results observed by Crawford in his thermal deazetation studies of labeled 4-ethylidene-1-pyrazolines,[13,14] exemplified below by the thermolysis of **11**.



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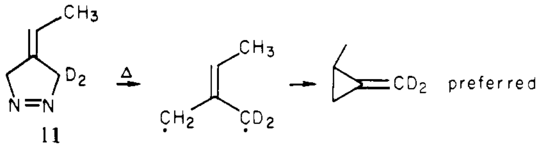
12

These results were rationalized via involvement of diazenyl allyl diradicals such as **12**, to the exclusion of TMM's. Crawford's mechanism will correctly predict both the 90:10 regiochemical preference as well as the observed 9:1 stereochemical preference. Moreover, this mechanism could potentially explain the regiochemical preferences observed by us in our deazetations of **3** and **4**.

Without belaboring the arguments for intermediacy of a TMM vs. a diazenyl allyl diradical and regardless of whether single C–N bond homolysis or synchronous N_2 extrusion occurs, suffice it to say that it is possible to rationalize Crawford's elegant results through the intermediacy of TMM's if one merely invokes initial formation from **11** of a stereochemically *distinct* TMM (i.e., **13**)



11

13

which cyclizes more rapidly than it loses identity by TMM conformational interconversion. Again subtle deviations from the symmetry of the parent (C_4H_6) TMM could give rise, either via E_a or $\Delta S^‡$ differences, to the observed preferred cyclizations.

In this mechanism it is assumed that the *initially* formed TMM is largely responsible for product formation. Such a TMM is perhaps most conveniently thought of as the planar TMM, although the only feature really required of the intermediate is that the stereochemistry of its methyl group be largely maintained prior to cyclization. Indeed *planar* TMM's have been demonstrated to be thermodynamically accessible[7,8] and it is still an unanswered experimental question as to whether non-sterically encumbered TMM's prefer planarity or orthogonality.

It is interesting to note that the regiochemistries for methylenecyclopropane formation from 4-methylenepyrazolines such as **3** and **4** are virtually identical whether the substituents be fluorine or methyl. It is not yet possible to unambiguously rationalize this remarkable coincidence. While steric arguments cannot be reasonably invoked since methyl and fluorine have distinctly different steric requirements, methyl and fluorine *do* have similar masses. However, it is premature to invoke the mass of the substituent as a key factor in determining relative rates of cyclization of TMM diradicals.

Conclusion

In conclusion, product studies for the thermal and photochemical deazetations of **3** and **4** are consistent with the intermediacy of trimethylenemethane intermediates. In the case of the thermal reaction, cyclizations of the TMM's to products are dominated by factors unrelated to the thermodynamic stability of these products. In the case of the photochemical reactions, the cyclizations of the TMM's are dominated kinetically by "hot" processes, some of which are unquenched even in solution, leading to virtually statistical ratios of the cyclization products.

Work is currently underway to further elucidate those factors which affect the thermodynamic and kinetic behavior of diradicals in general and more specifically of trimethylenemethanes.

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Table III. Product Ratios from Thermolysis of **3** in Solution at 150 °C

time, min	1	2	% conversion
20	59.69	40.31	78
30	59.54	40.46	89
40	59.61	40.39	95
60	60.03	39.97	>99
av	59.72	40.28	

Experimental

Deazetations of 4-(Difluoromethylene)-1-pyrazoline (3). Gas-Phase Thermolysis. After carefully purifying pyrazoline **3**[3] by distillation and vacuum transfer, 5 mm of pure material was expanded into a well-conditioned thermolysis vessel at 150–162 °C.[24] Samples were taken periodically and the product ratios were determined by GLPC analysis (7-ft × $^1/_8$-in. 10% ODPN, ambient, 20 mL/min). The two products obtained were the difluoromethylenecyclopropanes **1** and **2** which were identified by comparison of their GLPC retention times with authentic samples[1] and by ^{1}H NMR analysis of the thermolysis mixture. The order of elution was **2** and then **1**. At a particular pressure, the product ratios were found to be independent of time through many half-lives of reaction. Each ratio in this and subsequent experiments is an average of three GLPC analyses. A kinetic run at 15 °C, using CCl_4 as an internal standard, led to the determination of a rate constant for the deazetation of **3**, 1.73 (±0.09) × $10^{-3}/s^{-1}$.

Gas-Phase Photolysis. Into a 25-mL pyrex gas sample bulb with a Teflon Rotoflo stopcock was expanded 2 mm of pyrazoline **3**. Photolysis in a Rayonet Photoreactor gave three products which were identified by comparison of their GLPC retention times with those of authentic samples and by ^{1}by NMR analysis of the photolysis mixture from a larger scale reaction with use of a 500-mL gas sample bulb. The effect of adding the indicated pressure of argon is presented in Table I.

Solution Thermolysis. Into a number of 25-mL glass tubes containing 5 mL of degassed CCl_4 was condensed 12 mg (0.10 mmole) of pyrazoline **3**. The tubes were sealed under vacuum and heated at 150 °C for the times indicated in Table III.

Solution Photolysis. Into a 25-mL Pyrex gas sample bulb with a Teflon Rotoflo stopcock containing 5 mL of degassed CCl_4 was condensed 12 mg (0.10 mmol) of pyrazoline **3**. Photolysis of four identical samples in a Rayonet Photoreactor (350 nm) for 1, 2, 3, and 8 h gave virtually invariant product ratios. With conversion of **3** virtually complete in each run, these data indicate the stability of the product ratios to the photochemical conditions.

Deazetations of 4-(Fluoromethylene)-1-pyrazoline (4). Gas-Phase Thermolysis. Into a well-conditioned thermolysis vessel at 168.0 °C was expanded 1 mm of pyrazoline **4**. The product ratio was monitored with respect to time by GLPC analysis (20-ft × $^1/_8$-in. 20% DNP, ambient, 86 mL/min). Also the effect of added argon was determined at 10 min. The order of elution was **9** and then **10**. The results are presented in Table II.

Gas-Phase Photolysis. Into a 25-mL Pyrex gas sample bulb with a Teflon Rotoflo stopcock was expanded 2 mm of pyrazoline **4**. The bulb was then pressurized with the indicated amount of argon and the sample was irradiated in a Rayonet Photoreactor (350 nm). Analysis by GLPC (20-ft × $^1/_8$-in. 20% ODPN and 10-ft × $^1/_8$-in. 10% DNP in series, ambient, 25 mL/min) gave the product ratios presented in Table II.

Solution Thermolysis. Into a 30-mL glass tube containing 5 mL of distilled, degassed CH_2ClCH_2Cl was condensed 21 mg (0.210 mmol) of pyrazoline **4**. The tube was sealed under vacuum and heated at 140 °C for 1 h. An identical sample was heated for 2 h at 140 °C with no substantive difference in result. The product ratio for **9** and **10** is presented in Table II.

Solution Photolysis. Into a 30- mL Pyrex gas sample bulb equipped with a Teflon Rotoflo stopcock containing 5 mL of distilled, degassed CH_2ClCH_2Cl was condensed 21 mg (0.210 mmol) of pyrazoline **4**. Two identical samples were irradiated at 38 °C in a Rayonet Photoreactor (350 nm) for 1 and 2 h. There was no substantive difference in the two results. Analysis by GLPC (DNP) gave the product ratios for **9** and **10** indicated in Table II.

Acknowledgment. Support of this research in part by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 67884-63-3; **2**, 67884-64-4; **3**, 88766-66-9; **4**, 86770-87-8; **9**, 86770-88-9; **10**, 86770-89-0; nitrogen, 7727-37-9.

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[24] The pyrolysis apparatus has been described in detail elsewhere.[17]