The Gas-Phase Thermal and Photochemical Decomposition of Heterocyclic Compounds Containing Nitrogen, Oxygen, or Sulfur

SILVIA BRASLAVSKY† and JULIAN HEICKLEN*

Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pennsylvania 16802

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I. Introduction

The purpose of this article is to review critically the thermal and photochemical reactions of heterocyclic compounds in the gas phase. Reactions in condensed phases (solutions, neat liquids, or solids) will be referred to only when they are relevant to the gas-phase processes being analyzed. We do not intend to review the synthesis of these compounds unless the mechanism involved helps to understand the gas-phase reactions.

The photochemistry of heterocyclic compounds in general has attracted great interest, and two major reviews have appeared, one on the photochemistry of heterocycles by Reid,[1] and the other on photochemistry of three-membered rings by Bertonier and Griffin.[2] Both of them cover the literature until 1970. In 1972, in Volume 5 of the "Comprehensive Chemical Kinetics Encyclopedia" edited by Bamford and Tipper, three reviews appeared which dealt with the decomposition and isomerization of oxygen (Richardson and O'Neal[3]), nitrogen (Strausz et al.[4]), and sulfur (Strausz et al.[5]) compounds, including the heterocyclic compounds, in the three phases. The review on oxygenaed compounds by Richardson and O'Neal did not cover the photochemistry of the molecules. The three reviews discussed the literature up to 1969.

It is our main purpose to concentrate on the new data which appeared in the 1970s to systematize the gas-phase studies with special emphasis on the mechanistic aspect of the reactions taking place when the heterocyclic compounds are excited, either by means of heat or of light. It may be obvious, but nevertheless necessary, to point out that nowadays no review can ever hope to be comprehensive, and we apologize for any involuntary omissions. The work described is classified in terms of ring size and within this scheme discussion of saturated molecules normally precedes that of nonsaturated or partially aromatic systems.

II. Three-Atom Rings

A. One Heteroatom

1. Saturated

c-CH_2CH_2NH (c = cyclo). The primary processes in ethylenimine (aziridine) upon excitation by light were determined by Kawasaki et al.[6] by irradiating the compound with Xe (147.0 nm) and Kr (123.6 nm) resonance lines as well as photosensitizing the decomposition with excited Xe and Kr atoms. The products included C_2H_4, C_2H_6, CH_4, H_2, NH_3, the dimer of ethylenimino radicals, and small amounts of C_2H_2, C_3H_8, and n-C_4H_{10}. The primary processes were visualized as (1a–c).

$$\overline{\mathrm{CH_2CH_2N}}\mathrm{H} + h\nu \rightarrow \mathrm{CH_3} + (\mathrm{H_2CN}) \quad (1a)$$

$$\rightarrow \mathrm{C_2H_4} + \mathrm{NH} \quad (1b)$$

$$\rightarrow \mathrm{C_2H_2} + (\mathrm{NH_3}) \quad (1c)$$

The investigators found upon direct excitation the following quantum yields: $\phi_{1a} = 0.41$, $\phi_{1b} = 0.36$, and $\phi_{1c} = 0.028$ at the Xe line, and $\phi_{1a} = 0.13$, $\phi_{1b} = 0.22$, and $\phi_{1c} = 0.028$ at the Kr line. The quantum yields were slightly different if the sensitization method was used. Kawasaki et al.[7] confirmed the presence of

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† Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstrasse 34–36, D4330 Mülhein/Ruhr, West Germany.

NH radicals by detecting the emission from their excited states. No emission was observed for direct excitation by the Xe resonance line at 147.0 nm, but sensitization by $Xe(^3P_1)$ gave emission from $NH(A^3\Pi)$. Direct excitation by the krypton line at 123.6 nm produced emission from $NH(c^1\Pi)$ while sensitization by $Kr(^3P_1)$ produced both the $c^1\Pi$ and $A^3\Pi$ states of NH.

The above observations extended those of earlier studies done on the $Hg(6^3P_1)$ sensitized decomposition of aziridine at 253.7 nm.[8-10] The purpose of the Hg-sensitized studies was to produce NH radicals. The presence of these radicals during the mercury photosensitized decomposition of ethylenimine was confirmed spectroscopically by Callear and McGurk.[11]

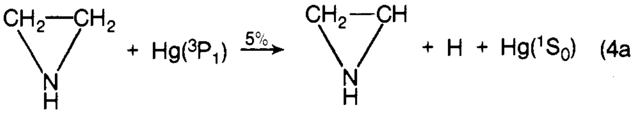
In the mercury-photosensitized studies major products were H_2, C_2H_4, N_2, and NH_3. It was not clear whether the N_2 came from reaction 2 or 3a, or both.

$$2NH \longrightarrow N_2 + H_2 \qquad (2)$$

$$2\overline{CH_2CH_2N}\cdot \longrightarrow N_2 + 2C_2H_4 \qquad (3a)$$

The NH_3 production was not clearly explained either. In the study performed in fast flow,[9] N_2 production was much less important than found under static conditions.[8] The minor products reported were also different in the two systems, being CH_4, C_2H_6, C_3H_8, C_2H_2, and C_4H_8 in the static system and HCN, CH_3CN, and CH_4 in the flow system. C_2H_2 was shown to come from the subsequent Hg-photosensitized decomposition of C_2H_4.[9] A reexamination of the static system[10] showed that C_3H_8, C_2H_2, and HCN were not produced, but that diaziridine, *N*-methylethylenimine, and *N*-ethylethylenimine were produced. Consequently there is some conflict regarding the minor products, and their importance may vary considerably with reaction conditions.

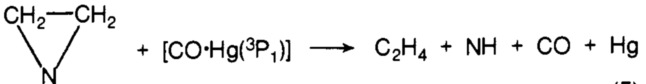
Jones and Lossing[9] proposed that the aziridine interacted with excited mercury $Hg(^3P_1)$ through two different paths (eq 4a, b).



(4a)

$$\xrightarrow{83-90\%} C_2H_4 + NH + Hg(^1S_0) \qquad (4b)$$

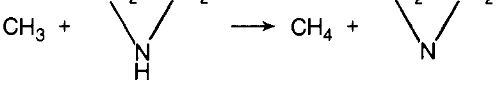
The addition of CO markedly enhanced the C_2H_4 quantum yield, but not that of propylenimine (a product of c-$NHCH_2CH$ radicals). They concluded that reaction 4a occurred directly, but that reaction 4b involved an electronically excited precursor. Presumably reaction 4b is enhanced if $Hg(^3P_1)$ is replaced by its complex with CO.



(5)

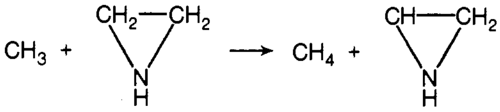
There is no further experimental evidence supporting this proposed mechanism for the CO effect. Furthermore the results of Klemm[10], who also studied the Hg-photosensitized decomposition of c-CD_2CD_2NH, indicated that the hydrogen atom detachment occurs preferentially from the nitrogen atom.

The different reactions of the CH and NH bonds in ethylenimine toward the H atom abstraction by a CH_3 radical have been studied by Gray and Jones[12] and by Klemm.[13] Gray and Jones, using c-CH_2CH_2NH and c-CD_2CD_2NH, deduced that for the reaction



(6a)

$\log k_{6a} = (7.17 \pm 0.05) - (4570 \pm 100)/\theta$ and for the reaction



(6b)

$\log k_{6b} = (8.44 \pm 1.48) - (10100 \pm 2800)/\theta$ for both reactions between 110 and 175 °C, where the rate coefficients are in M^{-1} s^{-1} units, the activation energies are in cal/mol, and $\theta \equiv 2.303RT$. The values found meant that almost all the abstraction occurred from the NH site.

Klemm[13] found $\log (k_{6a} + k_{6b}) = 7.86 - 5300/\theta$ between 120 and 260 °C in reasonable agreement with the results of Gray and Jones[12] and with the earlier value of $7.50 - 4800/\theta$ between 120 and 160 °C obtained by Brinton and Volman.[14] In his study Klemm also used c-CD_2CD_2NH and found that reaction 6a was at least 200 times as important as reaction 6b in his temperature range. He also discussed the relative importance of the reactions

$$2\overline{CH_2CH_2N}\cdot \longrightarrow N_2 + 2C_2H_4 \qquad (3a)$$

$$\longrightarrow (\overline{CH_2CH_2N}\cdot)_2 \qquad (3b)$$

and found partial evidence for the presence of the dimer. Neither C_2H_4 nor N_2 was found, thus indicating that reaction 3a was negligible compared to reaction 3b. (The production of the dimer of the ethylenimino radical and the absence of C_2H_4 were also interpreted by Kawasaki et al.[6] as a confirmation of the greater importance of reaction 3b over reaction 3a.) It was also concluded by Klemm that the reaction

$$\overline{CH_2CH_2N}\cdot \longrightarrow CH_3\cdot + HCN \qquad (7)$$

was unimportant because of the absence of HCN, but the analytical system used was not sufficiently good to rely on this conclusion.

The absence of C_2H_4 implies that during the direct or sensitized photolysis of ethylenimine, C_2H_4 is formed intramolecularly through reaction 4b. It also implies that reaction 2 must be the main source of N_2 production.

c-CH_2CH_2O. As in the case of aziridine, important primary photochemical processes give C_2H_4 or CH_3 radicals[15-18] in the photolysis of ethylene oxide (oxirane). The relative importance of the different primary processes was evaluated by Kawasaki et al.[18] They irradiated the epoxide with the Kr (123.6 nm), Xe (147.0 nm), Ar–N_2 (174.4 nm), and iodine (178.3, 179.9, 183.0, and 184.5) lines. The products of the photolyses were H_2, CO, CH_2O, CH_4, C_2H_4, C_2H_6, C_3H_8, n-C_4H_{10}, C_2H_2, and C_3H_6. It was found that the relative importance of the different processes

$$\overline{CH_2CH_2O} + h\nu \longrightarrow CH_3 + HCO\ (CO + H) \qquad (8a)$$

$$\longrightarrow O + C_2H_4\ (C_2H_2 + H_2) \qquad (8b)$$

$$\longrightarrow H_2 + (CH_2CO) \qquad (8c)$$

$$\longrightarrow CH_3CHO \qquad (8d)$$

$$\longrightarrow CH_2 + CH_2O \qquad (8e)$$

8a–e depended on the excitation energy. The results found are listed in Table I. The results Kawasaki et al.[18] obtained in the solid phase at 77 K indicated the same wavelength effect as in the gas phase.

In Table I the yield of reaction 8a was taken as unity. The investigators pointed out that reaction 8a which produces HCO can give rise to CO + H (reaction 9) instead, if the excess energy is high enough.

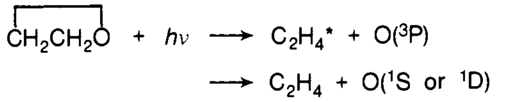
$$HCO^* \rightarrow CO + H \qquad (9)$$

TABLE I. Relative Importance of the Primary Photolytic Processes in Ethylene Oxide

Reaction	Primary products	147.0 nm[a]	174.4 nm[a]	178.3–184.5 nm[a]	180.0–200.0 nm[b]	$Hg(^3P_1)$ (253.7 nm[c]	Pyrolysis[d]
8a	$CH_3 + HCO$ $(H + CO)$	1.0	1.0	1.0	1.0	1.0	1.0
8b	$O + C_2H_4$ $(C_2H_2 + H_2)$	0.7	0.2	0.1	0.1–0.3	0.1	Trace
8c	$H + (CH_2CO)$	0.1	0.1		$\lesssim 0.2$	0.1	
8d	CH_3CHO	0.2				0.7	
8e	$CH_2 + CH_2O$	0.2				Trace	

[a] From Kawasaki et al.[18] [b] Calculated from Rocquitte.[17] [c] Calculated from Cvetanović. [d] From Benson[19] and references therein.

From a kinetic treatment of the data it was deduced that in reaction 8b the excess energy could be partitioned in two ways: to give excited C_2H_4 ($C_2H_4^*$) capable of decomposition or to give unreactive C_2H_4. This suggested that the two processes were:



$$\overline{CH_2CH_2O} + h\nu \longrightarrow C_2H_4^* + O(^3P) \qquad (8b')$$

$$\longrightarrow C_2H_4 + O(^1S \text{ or } ^1D) \qquad (8b'')$$

For $\lambda = 147.0$ nm, $\phi_{8b''}/\phi_{8b'} = 2.7$ was obtained. The excited ethylene produced in reaction 8b′ can undergo reactions 10 or 11.

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \qquad (10)$$

$$C_2H_4^* + M \rightarrow C_2H_4 + M \qquad (11)$$

The value $k_{10}/k_{11} = 0.0095$ Torr^{-1} was obtained. Ketene was postulated as a product of reaction 8c. A small quantity of this compound has indeed been found in the pyrolysis,[19] photolysis,[20] and mercury sensitization[16] of ethylene oxide. In the study of Kawasaki et al.,[18] however, ketene has a maximum excess energy of 5.7 eV so it would immediately decompose to CO and CH_2 by the reaction

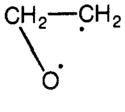
$$CH_2CO^* \rightarrow CH_2 + CO \qquad (12)$$

because $D\{CH_2{=}CO\}$ is 3.6 eV.[21] Kawasaki et al. discussed the effect of excitation energy on the decomposition of ethylene oxide. They concluded that the relative importance of reaction 8b, expulsion of the O atom, increased with the energy of excitation while that of reaction 8a, which required an intramolecular H migration, decreased with increasing energy. In the pyrolysis of ethylene oxide, CO, CH_4, and ethane (reaction 8a) were the main products and the yield of ethylene (reaction 8b) was very small.[22–26] In the mercury photosensitization the role of reaction 8d became quite significant, although reaction 8a was still dominant.[16]

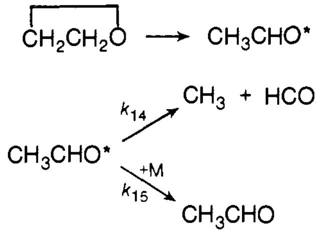
A comparison with the studies on the photolysis of ethylenimine can be made at this point. For that molecule, it was also found that an increase in the excitation energy decreases the importance of reaction 1a, which relatively enhances that of reaction 1b. That is, in both three-membered rings raising the input energy favors the expulsion of the heteroatom. The energy dependence of the ethylenimine NH expulsion is consistent with the thermal decomposition of ethylenimine compounds in the liquid phase[4] where only the products coming from the C–C fission in the ring were obtained. This fact can be explained by assuming that reaction 1b proceeds through a first stage in which the C–N bond is cleaved, and if the energy is high enough the other C–N bond is broken; otherwise the open $RNCR_2CR_2$ may be sufficiently stable to rearrange before decomposition or even be trapped.

The same processes occur when excited ethylene oxide is produced from the reaction of $O(^3P)$ with C_2H_4; the adduct isomerizes and then decomposes to CH_3 and HCO radicals.[27,28] Likewise the addition of NH to C_2H_4 in a low-temperature matrix gives ethylenimine,[29] but in the gas phase CH_3 radicals are produced. Therefore there is a significant similarity between the photolysis and Hg sensitization of ethylenimine and ethylene oxide and the decomposition of energy rich molecules formed in the reaction of C_2H_4 with NH or O atoms.

Reaction 8a can proceed through a biradical with the following structure



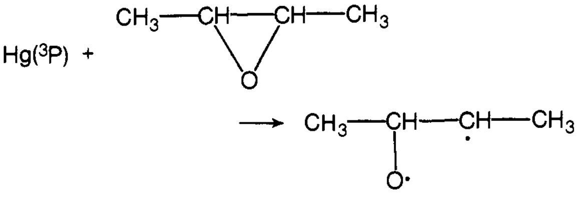
which could then undergo a H migration giving rise to CH_3CHO^* (an excited acetaldehyde molecule), which in turn could decompose into $CH_3 + HCO$. In the case of low excess energy the excited molecule could be deactivated easily to give ground-state CH_3CHO. The participation of an excited acetaldehyde intermediate was postulated by Neufeld and Blades[30] to explain the kinetics of the thermal reactions of ethylene oxide at 400 °C (reactions 13 to 15). This mechanism explained the previous results obtained by Lossing et al. [25]and Mueller and Walters.[23] In 1964, Benson[19] thoroughly analyzed the data from the pyrolysis of ethylene oxide and demonstrated the participation of the excited acetaldehyde species (CH_3CHO^*) which could be either be quenched or give $CH_3 + HCO$. He calculated the activation energy for the isomerization (eq 13) to be 57 kcal/mol and the lifetime of the excited acetaldehyde intermediate produced when ethylene oxide was pyrolyzed between 400 and 500 °C to be $10^{-8.5}$ s, so that at pressures ≥ 200 Torr, the predominant fate of the excited CH_3CHO^* is to be quenched. Benson postulated that the first process in the excited ethylene oxide was a C–O cleavage, giving the biradical.



$$\overline{CH_2CH_2O} \longrightarrow CH_3CHO^* \qquad (13)$$

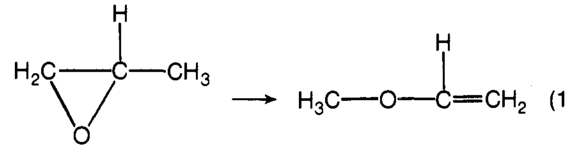
$$CH_3CHO^* \xrightarrow{k_{14}} CH_3 + HCO \qquad (14)$$

$$CH_3CHO^* \xrightarrow[k_{15}]{+M} CH_3CHO \qquad (15)$$



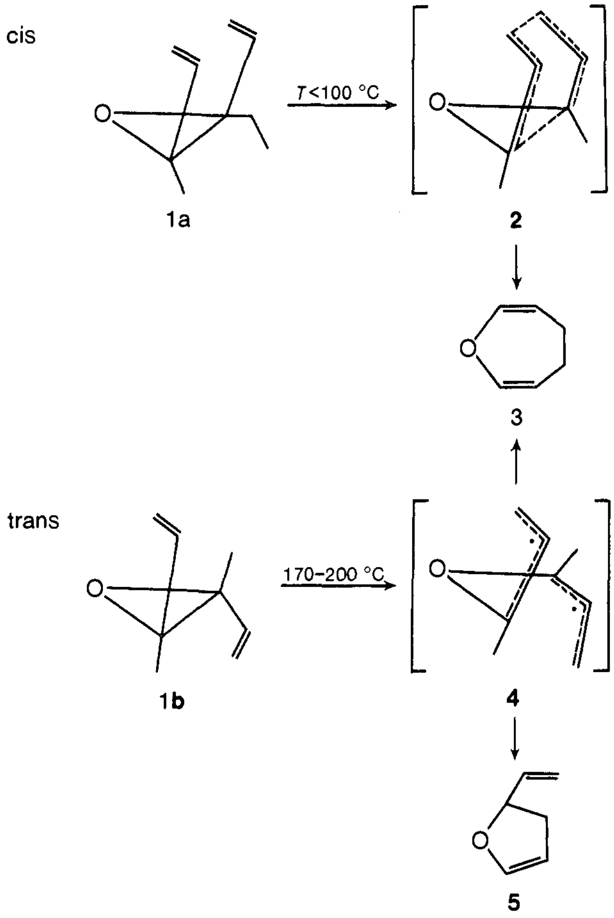
$$Hg(^3P) + CH_3CH(O)CHCH_3 \longrightarrow CH_3\overset{\cdot}{C}H(O\cdot)\text{—}\dot{C}HCH_3 \qquad (16)$$

Substituted Oxiranes. The possible biradical formation after C–O bond fission was discussed by Cvetanović and Doyle[31] in their study of the Hg-photosensitized decomposition of butylene oxide (reaction 16). The thermal decomposition of propylene oxide at 400–499 °C yields propionaldehyde as a major product.[32,33] The first-order rate expression for propylene oxide removal in the temperature range 402–459 °C is $k = 3.7 \times 10^{12} \exp\{-51900/RT\}$ s^{-1}.[33] On the other hand, Blades[34] found heterogeneous reactions contributing to the formation of propionaldehyde, acetone, and allylol (2-propen-1-ol), and he could not elucidate the mechanism of the decomposition of the oxirane. However, he found evidence for the homogeneous formation of methyl vinyl ether, which indicates a C–C cleavage (reaction 17)

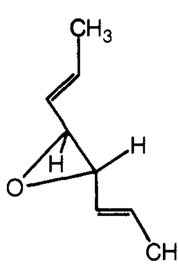


(17)

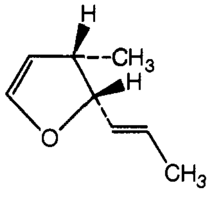
This kind of cleavage (the C–C of the oxirane ring) was also postulated to explain the results on the gas-phase ring expansions of the divinyl 1,2-epoxides studied by Vogel and Günther.[35] These divinyl 1,2-epoxides upon heating underwent the following reactions. In the case of the trans compound the seven-membered ring ether (4,5-dihydrooxepin) was obtained 30% of the time, and the five-membered ring ether (2-vinyl-2,3-dihydrofuran) was obtained 70% of the time independent of pyrolysis time and temperature between 170 and 200 °C. The rearrangements for both the cis and trans epoxides were homogeneous and first order. The investigators determined for the cis compound (**1a**) $\Delta H^{\ddagger} = 24.6$ kcal/mol and $\Delta S^{\ddagger} = -11.3$ cal deg^{-1} mol^{-1} and for the trans compound (**1b**) $\Delta H^{\ddagger} = 36$ kcal/mol and $\Delta S^{\ddagger} = -0.4$ cal deg^{-1} mol^{-1}. Taking into account these results they postulated a synchronous mechanism for the cis compound passing through the intermediate (**2**) and a biradical (**4**) mechanism for the trans oxide, but in both cases the cleaved bond was thought to be the C–C bond.



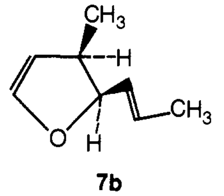
Pomelet et al.,[36] in order to examine this problem, studied the thermal decomposition of substituted vinyl epoxides, that is, **6**, in the vapor at 350 °C and found two products of ring expansion; one with retention of configuration **7a** and the other one with inversion of configuration **7b**. In both cases their results could be explained only if a C–C bond was cleaved, thus supporting the C–C fission previously postulated by Vogel and Günther.[35]



trans-**6**



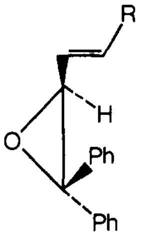
7a



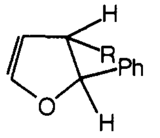
7b

This conclusion is based on the location of the substituents in the final product.

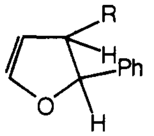
In a further effort to elucidate this point, Paladini and Chuche[37] studied by NMR the products of the gas-phase pyrolysis of the vinyl epoxide **8**. They studied the cis and trans compounds with different groups as R, including H, at temperatures lower and higher than 450 °C. At T <450 °C they observed two kinds of processes: (a) cis–trans isomerization of the epoxide and (b) formation of a dihydrofuranic compound (*trans*-**9** and *cis*-**9**). At T >450 °C the furanic compounds exclusively were formed. To explain their results they proposed C–C bond cleavage to give an ionic intermediate (**10**) in equilibrium with, for instance, the starting cis epoxide, which could give rise to either the furanic compound or the trans epoxide. The results obtained by Paladini and Chuche during this work could be explained again by a biradical mechanism following a C–C bond fission rather than an ionic intermediate.



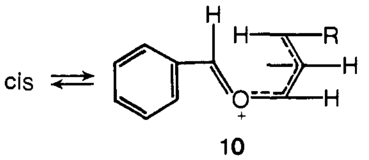
8



trans-**9**



cis-**9**



10

In 1970, Flowers and co-workers started a systematic study of thermal reactions of epoxides in order to decide what was the actual mechanism of epoxide decomposition. The first study concerned the thermal decomposition of 2,3-epoxy-2,3-dimethylbutane.[38] They hoped that in this compound, unlike ethylene oxide[25,30] and propylene oxide[34] in which the pyrolyses are complicated by primary and secondary radical reactions, the tetrasubstituted ethylene would be less susceptible to radical

TABLE II. Arrhenius Parameters for the Thermal Reactions of 2-Methyl-1,2-epoxypropane[a]

k_{19}	Log A (s^{-1})	E_a (kcal/mol)
Overall	13.66 ± 0.40	53.37 ± 1.25
19a	13.38 ± 0.18	52.86 ± 0.57
19b	13.56 ± 0.47	56.16 ± 1.46
19c	11.59 ± 0.67	49.86 ± 2.08
19d	13.52 ± 2.32	61.77 ± 7.16

[a] From Flowers and Parker.[39]

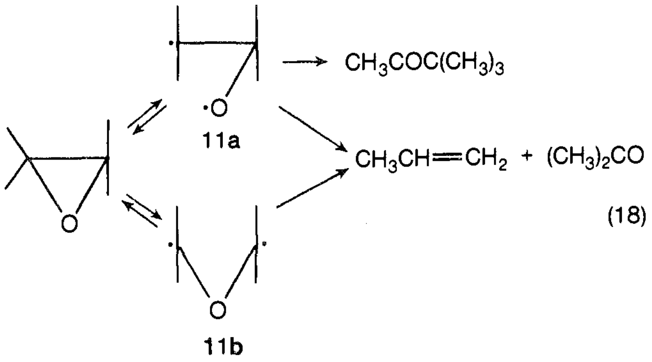
attack and thus provide clearer evidence for the mechanism of epoxide decomposition. Flowers et al.[38] found three competing, first-order, homogeneous nonradical reactions. The temperature range used was 388 to 456 °C. The products monitored were 3,3-dimethylbutan-2-one, propene, and 2,3-dimethylbut-3-en-2-ol. The values determined for the rate constants for the formation of the products were

$$k\{CH_3COC(CH_3)_3\} = 10^{13.83\pm0.43}\exp\{(-56700 \pm 1360)/RT\}\ s^{-1}$$

$$k\{C_3H_6\} = 10^{14.77\pm0.76}\exp\{(-59220 \pm 2400)/RT\}\ s^{-1}$$

$$k\{\text{alcohol}\} = 10^{10.88\pm0.65}\exp\{(-47500 \pm 2050)/RT\}\ s^{-1}$$

To produce 3,3-dimethylbutan-2-one requires C–O bond cleavage, but C_3H_6 (+ acetone) could be produced either through C–O or C–C bond breaking (eq 18). The mechanism for the formation of 2,3-dimethylbut-3-en-2-ol was more difficult to explain. The investigators preferred the **11a** intermediate as a route to the alcohol although they did not discard a concerted reaction from the epoxide.



(18)

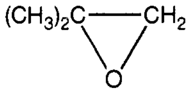
The investigators made a generalization of their scheme and applied it to the other epoxides studied. By estimating the heats of formation of the different intermediates using group additivity, they argued that in ethylene oxide, the C–O fission was favored over the C–C fission on thermodynamic grounds. In the propylene oxide case, on the contrary, the intermediate **11b** could be formed, thus explaining the results obtained by Blades.[34] As for the butane epoxide under study, Flowers et al.[38] could not decide whether one or both intermediates (**11a** and **11b**) participated.

A study performed by Flowers and Parker[39] was on the thermal gas-phase reactions of 1,2-epoxy-2-methylpropane. The temperature range used was 377–436 °C and the pressure was between 5.3 and 61.6 Torr. Through a careful kinetic study they determined the rate constants of the four major first-order, homogeneous, nonradical and presumably unimolecular reactions (eq 19a–e). The Arrhenius parameters obtained are listed in Table II.

A similar study was performed on the thermal gas-phase reactions of *cis*- and *trans*-2,3-epoxybutane.[40] The temperature range used was 395–667 °C. The cis–trans isomerization occurred at a much slower rate than the structural isomerization to butan-2-one, but-3-en-2-ol, ethyl vinyl ether, and isobutyraldehyde, the last two compounds being produced almost exclusively from the cis isomer. It was found again that the reactions were all homogeneous, first order, nonradical, and accounted for more than 80% of the observed decomposition. The Arrhenius parameters were determined and are listed in Table III.

TABLE III. Arrhenius Parameters for the Thermal Gas-Phase Reactions of *cis*- and *trans*-2,3-Epoxybutane (from Flowers and Parker[40])

k for reaction	Log A (s^{-1})	E_a (kcal/mol)
cis → trans	14.59 ± 0.53	61.83 ± 1.68
cis → butan-2-one	13.60 ± 0.21	56.32 ± 0.66
cis → but-3-en-2-ol	12.18 ± 0.94	53.99 ± 2.99
cis → ethyl vinyl ether	12.94 ± 0.96	55.23 ± 3.04
cis → isobutyraldehyde	12.99 ± 0.62	55.97 ± 1.97
trans → cis	14.67 ± 0.49	63.01 ± 1.59
trans → butan-2-one	14.24 ± 0.65	59.29 ± 2.12
trans → but-3-en-2-ol	12.73 ± 0.81	55.65 ± 2.60
trans → ethyl vinyl ether	14.23 ± 0.75	62.78 ± 2.44



$\longrightarrow (CH_3)_2CHCHO$ (19a)
isobutyraldehyde

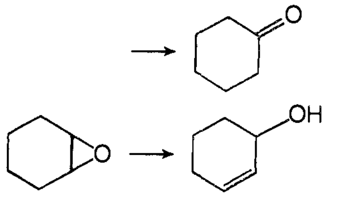
$\longrightarrow CH_3OC(CH_3){=}CH_2$ (19b)
isopropenyl methyl ether

$\longrightarrow CH_2{=}(CH_3)C{-}CH_2OH$ (19c)
2-methylprop-2-en-1-ol

$\longrightarrow CH_3COCH_2CH_3$ (19d)
butan-2-one

$\longrightarrow$ other products (19e)

The ethyl vinyl ether must occur through C–C cleavage. Because of the low A factors for but-3-en-2-ol formation, particularly from the cis compound, the investigators suggested that this product was formed via a concerted four-center activated complex. However, they favored C–O fission to explain the other products.



(20a)

(20b)

$\longrightarrow$ other products (20c)

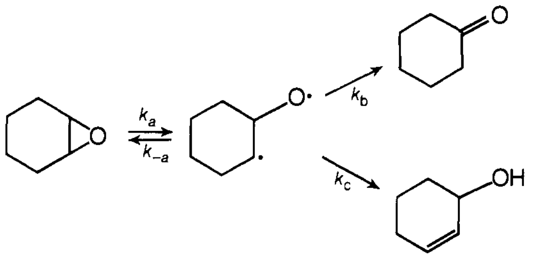
Flowers et al.[41] undertook the study of the thermal gas-phase isomerization of 1,2-epoxycyclohexane between 407 and 467 °C and from 1.6 to 7 Torr. The investigators made the remark that this was the most reliable of all the epoxide pyrolyses so far studied because of the absence of side reactions, secondary decompositions, or heterogeneous effects. Two of the products found accounted for 97% of the reactant decomposition. The two main reactions were (20a) and (20b) and the determined rate constants were

$$k_{20a} = 10^{14.58\pm0.35}\exp\{(-60300 \pm 1100)/1.987T\}\ s^{-1}$$

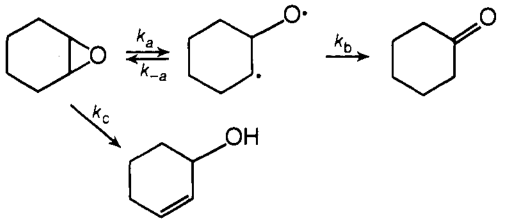
$$k_{20b} = 10^{13.11\pm0.41}\exp\{(-55800 \pm 1300)/1.987T\}\ s^{-1}$$

The investigators could not find any product corresponding to the C–C bond fission route. The explanation they gave was that the conrotatory motion that had to accompany the C–C fission was not possible in the molecule under study. If the C–O bond fission actually was the main primary process upon thermal excitation of the molecule, there still remained the question of whether Scheme I or II was taking place.

SCHEME I



SCHEME II



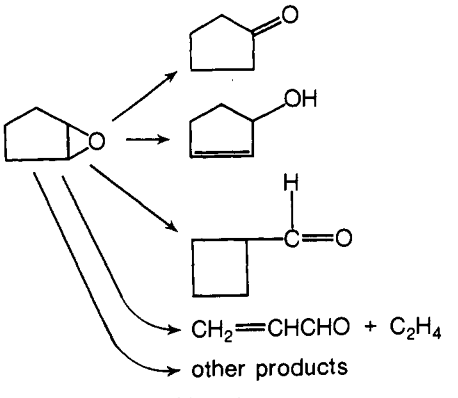
In Scheme I the alcohol is formed through the biradical, whereas in Scheme II, H atom migration accompanies the ring opening in a concerted step. Flowers et al. could not make a distinction between these two schemes, but based on the Arrhenius parameters they preferred Scheme II for alcohol formation. In order to distinguish between the two schemes, a study of the therml isomerization of 1,2-epoxycyclohexane-*3,3,6,6*-d_4 at 404–473 °C was performed.[42] A series of rate constants and the corresponding Arrhenius parameters were determined, but it was still not possible to decide which of the schemes was taking place. Since the deuteration reduced the rate of alcohol formation, the investigators concluded, however, that if there were a common intermediate for both products (Scheme I), then the rate of ring closure (k_{-a}) should be much faster than the rate of H transfer to give the ketone and the alcohol.

Flowers and Penny[43] studied the thermal decomposition of 6-oxabicyclo[3.1.0]hexane between 397 and 469 °C and 2 to 28 Torr pressure. The major products found were cyclopentane and cyclopent-2-en-1-ol accounting for 97% of the primary reaction products. Again both products were found to be formed by first-order, homogeneous, nonradical processes with rate constants

$$k\{\text{cyclopentanone}\} = 10^{14.16\pm0.11}\exp\{(-57500 \pm 400)/1.987T\}$$

$$k\{\text{alcohol}\} = 10^{13.56\pm0.16}\exp\{(-57900 \pm 500)/1.987T\}$$

The general scheme proposed is shown in eq 21a–e. Reactions 21a and 21b were determined to be first order, homogeneous, and not affected by radical inhibitors.



(21a)

(21b)

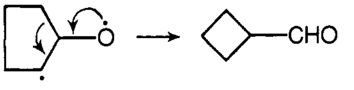
(21c)

$CH_2{=}CHCHO + C_2H_4$ (21d)

other products (21e)

As for the mechanism taking place, they again postulated two possibilities for reactions 21b analogous to Schemes I and II for the six-membered ring compound and could not decide which was operating. Dihydropyran which could come from a C–C cleavage was not found. However, this strained four-membered ring compound would decompose to propenal and ethylene owing to the high temperature used in the study so that it would not be seen. It could have been produced with k_{21c}(460 °C) < 1.7×10^{-5} s^{-1}.

Since the cyclobutane carbaldehyde was not formed in solution, it was concluded that it probably is produced via a concerted reaction of the biradical (reaction 21c′) instead of a C–C cleavage mechanism.



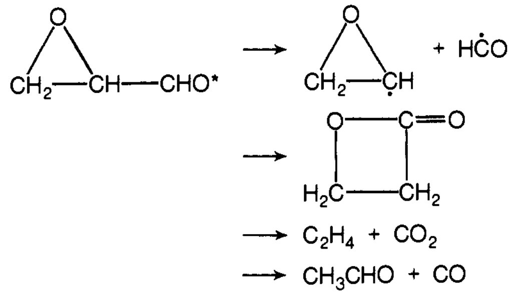
(21c′)

The evidence so far obtained indicates that both C–O and C–C bond fission occur in epoxide pyrolysis, and that concerted mechanisms may also occur. For unsubstituted alkyl-substituted epoxides C–O cleavage is favored to form aldehydes, ketones, and possibly alcohols. However for vinyl or phenyl substitution C–C bond fission is preferred to form ethers and ring-expanded compounds.

There are still two other studies performed on the epoxide gas-phase reactions that bear some interesting features. One is the isolation and purification of tetrafluoroethylene oxide, made in 1964, by Caglioti et al.[44] during the oxidation of C_2F_4 by molecular O_2. However, the compound was very unstable and isomerized to trifluoroacetyl fluoride, CF_3CFO, thus confirming that the C–O bond fission mechanism was operative, followed by an unusual F migration.

Biradical formation surely must occur in the pyrolysis of tetrafluoroethylene oxide, since its thermal decomposition gives $CF_2O + CF_2$.[45] Later Lenzi and Mele[45] showed that the isomerization was heterogeneous and dominant at low temperatures. However at higher temperatures (>40 °C) a gas-phase decomposition to $CF_2O + CF_2$ occurred with a high-pressure activation energy of 31.6 kcal/mol.

The other study is the photolysis of glycidaldehyde.[46] The wavelength used was 313 nm and the temperature range 77 to 127 °C. The primary processes the molecule underwent are given in eq 22a–d. The C=O group is responsible for the electronic transition involved, and reaction 22a is similar to the one undergone by aliphatic aldehydes. Reactions 22c and 22d also involve a change in the charge distribution of the C=O bond in the excited state. Reaction 22b is the only one taking place in a way similar to the other epoxide compounds, because a C–O bond has to be cleaved while another C–O bond is being formed. In the study, quantum yields of the different products were reported and a tentative evaluation of the relative importance of the different primary processes was made but the results were too limited to permit the formulation of a conclusive mechanism.



(22a)

(22b)

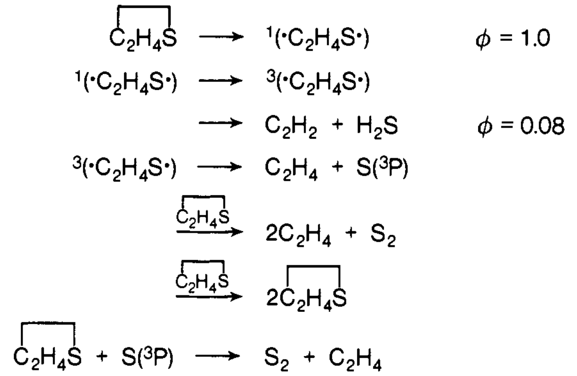
$\longrightarrow C_2H_4 + CO_2$ (22c)

$\longrightarrow CH_3CHO + CO$ (22d)

Thiiranes. Since Strausz et al.[5] reviewed the unimolecular homogeneous decompositions and isomerizations of sulfur compounds, very little has been published on the gas-phase reactions of thiiranes (episulfides).

The basic difference between the behavior of the thiiranes with the carbocyclic and oxoheterocyclic compounds is that the thio compounds principally undergo desulfurization. For instance, ethylene episulfide yields sulfur and C_2H_4 upon irradiation[47] or heating at temperatures below 250 °C.[48] This compound did not isomerize to thioacetaldehyde which would be analogous to the already discussed reactions 8a and 8d undergone by oxirane.

The difference in behavior observed for the oxoheterocyclic compounds with respect to the sulfur analogs has been attributed[49] to the much larger enthalpy changes which accompany transformations of the C—O single bond to double bond as compared with that for C—S → C═S bond transformation. There have not been enough wavelength studies with the thio compound, however, to thoroughly compare the ethylenimine, oxirane, and thiirane behavior. While studying the photolysis of thiirane with 253.7-nm radiation, Sidhu et al. (unpublished) found C_2H_4 accounted for 95% of the total products at low conversions with H_2, CH_4, and C_2H_2 as minor products. From the pressure dependence of the quantum yield of ethylene, the flash spectroscopic observations of $S_2(X\ {}^3\Sigma_g^-)$ as the only detectable transient, and conventional scavenging with olefins which indicated the presence of $S(^3P)$ at very low pressures of thiirane, the mechanism of eq 23–27 was outlined, where the super-scripts 1 and 3 mean singlet and triplet state, respectively. Reaction 24 was found to be very rapid and pressure independent. The investigators reported finding that the biradical $\cdot C_2H_4S\cdot$ was sufficiently long lived to be trapped by olefins and that the S atoms were in their ground state. In the case of the pyrolysis of the ethylene episulfide, however, no S atoms were found.[48] The thermolysis below 250 °C was found to be homogeneous and first order, giving rise to olefin and sulfur in stoichiometric yields. At temperatures above 250 °C a second decomposition path took place giving vinyl mercaptan and another mode of decomposition, probably a molecular split into $H_2S + C_2H_2$.

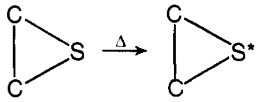


$$C_2H_4S \longrightarrow {}^1(\cdot C_2H_4S\cdot) \qquad \phi = 1.0 \tag{23}$$
$${}^1(\cdot C_2H_4S\cdot) \longrightarrow {}^3(\cdot C_2H_4S\cdot) \tag{24a}$$
$$\longrightarrow C_2H_2 + H_2S \qquad \phi = 0.08 \tag{24b}$$
$${}^3(\cdot C_2H_4S\cdot) \longrightarrow C_2H_4 + S(^3P) \tag{25}$$
$$\xrightarrow{C_2H_4S} 2C_2H_4 + S_2 \tag{26a}$$
$$\xrightarrow{C_2H_4S} 2C_2H_4S \tag{26b}$$
$$C_2H_4S + S(^3P) \longrightarrow S_2 + C_2H_4 \tag{27}$$

At low temperatures ($T < 250$ °C) the activation energy was 40.2 kcal/mol. Since this value was lower than the enthalpy change for the following reaction

$$\text{episulfide} \longrightarrow \text{ethylene} + S(^3P) \tag{28}$$

which is 58 kcal/mol, this reaction could not occur in the primary step. Furthermore the addition of pentene showed that sulfur atoms were not produced. The other experimental result found was that inert gases suppressed the reaction, a fact that is not compatible with an adiabatic reaction. To explain these results Lown et al.[48] postulated the production of an intermediate (**12**, eq 29) which can then react with ordinary thiirane (eq 30). The intermediate is thought to be an excited π thiacyclopropane located at not more than 40.2 kcal/mol above the ground state. It was concluded that the heating induced a promotion of one of the C–S bonding electrons into an antibonding orbital. It was further assessed that this excited state should be the lowest (n,σ^*) triplet of the episulfide.[5] It was also found that during pyrolysis of thiirane, isomerization of olefins was induced and this was taken as evidence for the production of the triplet state of thiirane.[50] It is necessary to point out that the triplet must be different from the one giving rise to $S + C_2H_4$ through reaction 25 during the photochemical studies, since in the thermal decomposition, absence of sulfur atoms was claimed. This observation seems to be confirmed by the calculations carried out by Hoffmann et al.[51] which indicated different excited states when sulfur atoms add to olefins or in thiirane pyrolyses. This conclusion seems to be consistent with the difference in behavior of the photolytically and thermally produced excited states. Ab initio molecular orbital calculations performed by Strausz and co-workers[52,53] support the location of the lowest thiirane (n,σ^*) triplet state at 40 kcal/mol, which agrees with the activation energy experimentally determined, and thus supports the hypothesis of triplet participation.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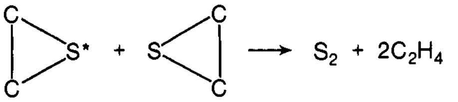
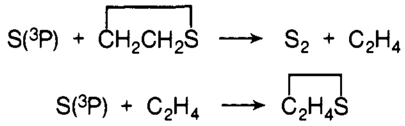


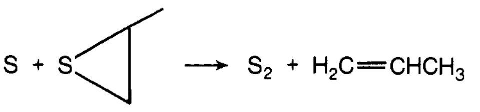
$$\longrightarrow S_2 + 2C_2H_4 \tag{30}$$

The flash photolytic study[54] of $c\text{-}C_2H_4S$ (ethylene episulfide) was also performed, and the proposed mechanism was the same as the one outlined for continuous irradiation. During this study the investigators said that reaction 27 should be a very rapid reaction. This was confirmed experimentally afterwards in two separate studies.[55,56] In the first one, the relative importance of the reactions



$$S(^3P) + CH_2CH_2S \longrightarrow S_2 + C_2H_4 \tag{31}$$
$$S(^3P) + C_2H_4 \longrightarrow C_2H_4S \tag{32}$$

was determined, and k_{31} was calculated to be $(3.0 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 27 °C. In the second one, another method was employed and the Arrhenius parameters for the ratios k_{32}/k_{31} and k_{32}/k_{33} were determined



$$S + S\text{(ring)} \longrightarrow S_2 + H_2C{=}CHCH_3 \tag{33}$$

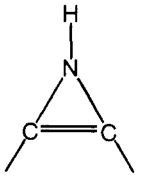
resulting in

$$E_{32} - E_{31} = 1.8 \text{ kcal/mol}$$
$$E_{32} - E_{33} = 2.1 \text{ kcal/mol}$$
$$A_{31}/A_{32} = 8.3$$
$$A_{33}/A_{32} = 8.4$$

In related work on the photolysis of tetraphenylethylene episulfide performed in liquid phase,[57] it was found that sulfur extrusion was also the main process, and that the C–C cleavage was negligible.

2. Unsaturated

The three so-called antiaromatic three-membered rings, 2-azirine (**13**), oxirene (**14**), and thiirene (**15**), have been postulated as intermediates in several reactions,[29,49,56,57] but because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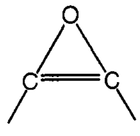
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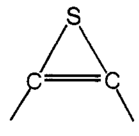
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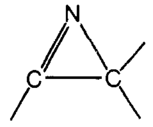
of their great ring strain are very unstable and have never been isolated as individual compounds, neither they nor their derivatives. This is surprising because the almost equally strained 1-azirine (**16**) is a very well-known ring system and many derivatives have been isolated and characterized so far.[58] The difference in stability between compounds derived from ring **13** and those derived from ring **16** was attributed to an unfavorable electronic situation in the 2-azirine compounds.[58]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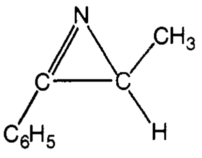
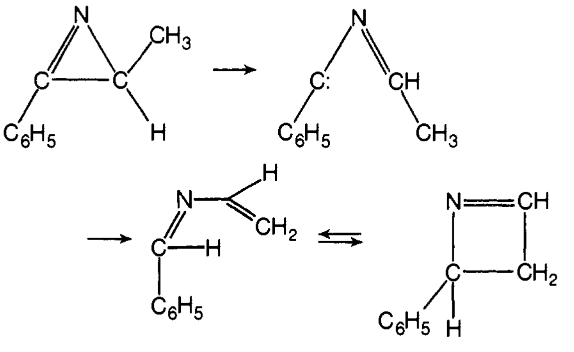
In the study performed by Strausz et al.,[49] on the addition of sulfur atoms to triple bonds, the formation of thiirenes was postulated as the primary adduct between S(^{3}P) and acetylene based on a transient absorption spectrum. The final product is thiophene, presumably formed from the rapid reaction of the thiirene with another acetylene molecule.

Dewar and Ramdsen,[59] using the semiempirical methods MINDO/3 and NDDO, calculated the relative stability of rings **13–15** compared with the cyclopropene ring and concluded that these antiaromatic rings lie in local energy minima of their potential energy surfaces and therefore are likely to exist as intermediates, though with very short lifetimes.

There is a gas-phase study on 1-azirine (**16**) compounds by Wendling and Bergman[60] who found that a C–C bond cleavage occurred during the thermolysis of these compounds, giving rise to products previously unobserved in both thermal and photochemical azirine decompositions in the liquid phase. The flow pyrolysis at 565 °C, under 1 atm of He, of the following compound was performed:

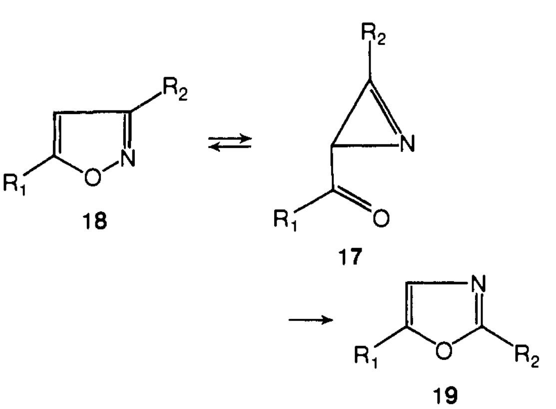


To explain their results the investigators proposed the following scheme and suggested that the presence of stabilizing groups on carbon 2 tends to induce fragmentation of the C–C bond, while substitution on carbon 3 enhances C–N bond fission (eq 34).



(34)

The 1-azirine derivatives have been the object of several studies performed in solution.[61,62] It is of some interest to our further discussion on the rearrangements of five-membered heterocyclic compounds to point out some of the conclusions reached during the liquid-phase studies of 1-azirines. The irradiation of compound **17** (R_1 = 1′-$C_{10}H_7$ (1′-naphthoyl) and R_2 = Ph) within its long wavelength absorption band (λ_{max} 304 nm) resulted in phototransformation only to the isoxazole compound (**18**), while absorption in the short wavelength band (λ_{max} 228 nm) produced the oxazoles **19** and **18** in a 3:1 ratio. Intermediate ratios of **19** to **18** were found in the 275- to 285-nm region of overlap of the two band systems.[61] Padwa et al.[62] during a study of the 2-phenyl-substituted 1-azirines found similar results, since heating of compound **20** resulted in the isooxazole **21**, while its irradiation resulted only in the oxazole **22**. According to Singh et al.[61] the high-energy system, giving rise to oxazoles, would come from a higher energy state associated with the nitrogen (n,π^*) transition that leads to an azirine C–C cleavage and subsequent rearrangement to the oxazole. A lower energy state, associated with the carbonyl (n,π^*) transition, caused electronic reorganization promoting concerted rearrangement to isoxazole. The thermal rearrangement would be similar to the photochemical low-energy system. This discrimination of chromophoric groups in a molecule has been done several times in the last few years, and helps us to understand the different ways a molecule can decompose for excitation with different energy. We will see this again in the five-membered ring case (vide infra).



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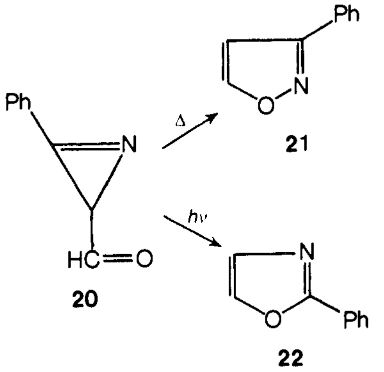
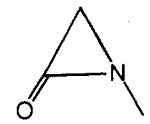


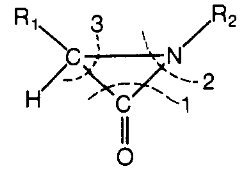
(36)

3. *α-Lactams*

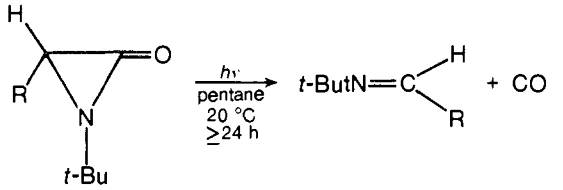
The so called α-lactams or aziridinones, derived from the following ring system,



are very unstable compounds and undergo rapid thermal isomerization. The stabilized ones bear large groups on the N or on the C atom[63] and are not suitable for gas-phase studies. The substituted α-lactams, when studied in liquid phase, can undergo three bond cleavages along the lines 1, 2, and 3. By studying the



electron impact induced fragmentation of several lactones, Talaty et al.[64] concluded that the cleavage along 1 was most important, that fission along 2 was negligible, and that fission along 3 was noticeable only when R_2 was the adamantyl radical. This result was in agreement with a study performed also in the liquid phase (pentane) irradiation of the following class of compounds[65]

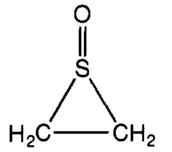


(37)

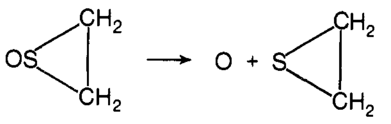
The investigators obtained the imine as the major product in sharp contrast with the thermal decomposition (also in the liquid phase) studied earlier[66] which did not give CO as a product, but gave instead a carbonyl compound and a cyanide or isocyanide.

4. Sulfones and Sulfoxides

During a vapor-phase study of the pyrolysis of ethylene episulfoxide triplet ground state ($^3\Sigma^-$), sulfur monoxide was identified by microwave spectroscopy, and no SO($^1\Delta$) could be detected by EPR.[67,68]

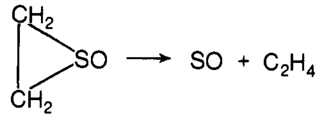


The decomposition into O and $(CH_2)_2S$ (reaction 38) was ruled out since ethylene episulfide was not found in appreciable quantities.



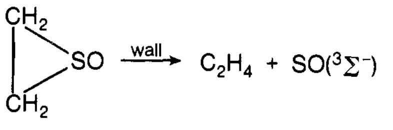
(38)

If reaction 39 is the first step of the reaction mechanism, and SO is formed in its triplet ground state ($^3\Sigma^-$), then there must be some mechanism to account for the spin conservation violation which takes place during this step.



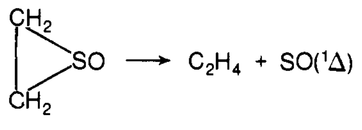
(39)

Saito[67,68] suggested a heterogeneous decomposition (reaction 40) of ethylene episulfoxide in order to release the spin conservation rule.



(40)

Breckenridge and Miller,[69] however, supported the hypothesis of the product being singlet ($^1\Delta$) SO in Saito's study and postulated reaction 41 as the primary step, followed



(41)

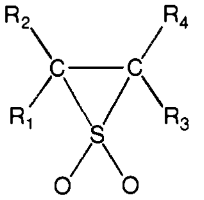
by rapid wall deactivation of SO($^1\Delta$) (eq 42).

$$SO(^1\Delta) \xrightarrow{\text{wall}} SO(^3\Sigma) \qquad (42)$$

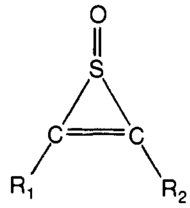
They ascribed the claimed lack of detection of SO($^1\Delta$) by EPR to technical problems.

The hypothesis of SO($^1\Delta$) being produced during the decomposition of thiirane oxide was rejected on thermochemical grounds by Lemal and Chao,[70] since Hartzell and Paige[71] had shown the activation energy for decomposition to be 35 kcal/mol in chlorobenzene. This leaves SO($^3\Sigma^-$) production as the only possible alternative for the primary step.

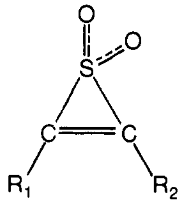
The cyclic saturated sulfones



are very unstable compounds and have been extensively studied in liquid phase[5,72] but, maybe because of their instability, there is no report of their behavior in the gas phase to our knowledge. The thiirene oxides (**23**) and dioxides (**24**) are the first examples of isolated three-membered ring heterocyclic compounds with the double bond opposite to the heteroatom. They have been synthesized[73,74] and some of their properties have been studied in the gas phase.

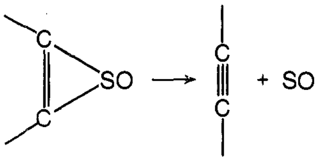


23

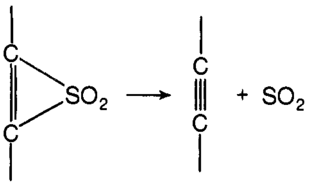


24

Vouros and Carpino[75] and Vouros[76] studied the electron impact and chemical ionization induced fragmentation of both compounds **23** and **24** with different substituents on the carbon atoms, both under high and low ionization conditions. They found that the most important decomposition path was reaction 43 for the sulfoxides and reaction 44 for the sulfones, giving rise to the substituted acetylene ion and SO in the first case, and the same ion and SO_2 in the second one.



(43)



(44)

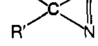
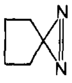
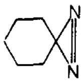
It is important to point out that the decomposition of all the three-membered ring sulfones and sulfoxides so far studied in the gas phase yield the SO or SO_2 moiety in the primary step, plus either the olefin if they are saturated or the acetylene if they are not saturated.

B. Two Heteroatoms

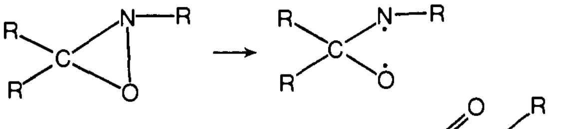
1. Oxaziranes

Apart from the pioneering work on the synthesis and reactions of oxaziridines (oxaziranes) by Emmons[77] in which the gas-phase pyrolyses of several different compounds of this family were performed, there apparently is no further study on the gas-phase behavior of these interesting compounds. Emmons found that at a temperature between 250 and 300 °C, depending on the particular compound, the oxaziridines (oxaziranes) decomposed

TABLE IV. High-Pressure Limits of Arrhenius Parameters of Diazirine Thermal Decompositions in the Gas Phase

		Log A, s^{-1}	E (kcal/mol)	Ref
R	R'			
F	F	13.4	32.5	88
C_2H_5	C_2H_5	13.73	31.89	87
		13.40	30.50	87
		13.34	30.87	87
Cl	CH_3	14.14	31.07	91
Cl	C_2H_5	13.99	30.45	89
Cl	n-C_3H_7	13.98	30.98	89
Cl	i-C_3H_7	14.01	30.59	89
Cl	t-C_4H_{10}	13.36	29.50	89

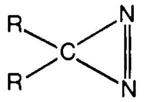
according to reaction 45 in which a cleavage of the N–O bond takes place together with or followed by a migration of one of the groups from the ring carbon to the nitrogen of the ring.


(45)

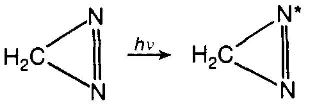
It is worth noting that oxaziridines are thermally labile and their isolation is sometimes difficult. In some photochemical studies of these compounds performed in the liquid phase, the products may be the result of thermal rather than photochemical reactions of the unstable ring.[2]

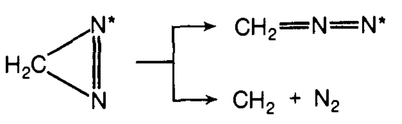
2. Diazirines

Diazirine and its derivatives have been the object of several



studies because of the possibility of their use as a source of carbenes, either by photolysis or by pyrolysis. A very complete review on the photolysis of diazirine and its derivatives appeared in 1966.[78] Though it was mainly devoted to the photochemistry of these compounds, it also discussed the pyrolyses when that helped to understand the photolytic behavior. At the time the review was written the photochemistry of diazirine was explained with a mechanism including the following as the main reactions


(46a)


(47a)

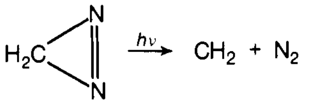
(47b)

$$CH_2{=}N{=}N^* + M \rightarrow CH_2{=}N{=}N + M \quad (48)$$

$$CH_2{=}N{=}N^* \rightarrow CH_2 + N_2 \quad (49)$$

This mechanism was based on a study performed by Amrich and Bell[79] who photolyzed from 5 to 30 Torr of diazirine in the presence of N_2 at 0 to 600 Torr with light of 320 nm. The presence of diazomethane ($CH_2{=}N{=}N$) was detected but it accounted only for 10% of the quantum yield of the diazirine disappearance which was 2, thus apparently setting a lower limit of 0.2 for the ratio k_{47a}/k_{47b}. Therefore isomerization to diazomethane apparently accounted for at least 20% of the primary decomposition of diazirine.

Photoisomerization of diazirines to diazo compounds has been observed in other photolyses of substituted diazirines, specifically in the liquid phase,[80] but its occurrence in the case of diazirine itself presents some problems, according to Frey's calculations. Considerations of the energetics of the system made Frey[78] suggest the possibility of the production of triplet diazomethane. Frey also pointed out that Moore and Pimentel,[81] from their experiments on photolysis of diaziridine in a nitrogen matrix enriched in ^{15}N, concluded that the primary reaction was


(46b)

followed by the recombination of the CH_2 produced with the N_2 of the matrix, which ruled out the isomerization to diazomethane. Furthermore they found no diazomethane in gas-phase photolyses. There is, indeed, a contradiction between these results and those obtained by Amrich and Bell,[79] and it is not clear whether reactions 47a and 48 are occurring in the system and whether the CH_2 biradical comes from the excited diazirine (reaction 47b) or from the excited diazomethane (reaction 49).

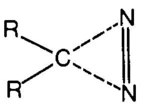
The problem of the electronic state of the excited molecule is not resolved either, although there is evidence that at the absorption band used (280 to 330 nm) the diazirine undergoes an allowed ($\sigma \rightarrow \pi^*$) transition.[82] This band seems to be common to all the diazirines so far studied. The CH_2 produced from diazirine photolyses shows approximately the same discrimination in its attack on primary and secondary C–H bonds as the CH_2 from ketene photolysis and is more selective than the CH_2 from diazomethane photolysis in spite of the fact that the total energy in the CH_2 from diazirine and diazomethane photolysis is about the same.[78] The reason for this has not yet been established, but presumably it reflects different distributions of electronic, vibrational, rotational, and translational energy in the CH_2 species from the two isomeric CH_2N_2 compounds. Mitsch[83,84] has shown that photolysis of c-$CF_2N{=}N$ gives CF_2 radicals, and Mitsch and Rodgers[85] have argued that photolysis of all the dihalodiazirines gives the corresponding dihalomethylene in its singlet $^1\Delta$ state.

Many other diazirines have been photolyzed in the gas phase,[78,85,86] and photochemical behavior can be explained with the mechanism consisting of three primary steps: (1) photoisomerization of a diazo compound which may be electronically or vibrationally excited (it can undergo further deactivation or give rise to N_2 and a carbene); (2) direct split to N_2 and carbene (without the intermediate diazo compound); (3) molecular split to an olefin and N_2.

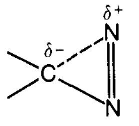
In the elementary step 2 (direct split to N_2 and carbene) two different carbenes can be formed. One would be triplet diradicals of fairly long lifetimes, and the other would be the singlet which would isomerize rapidly to vibrationally excited ground-state olefins which can either decompose, isomerize, or be deactivated.

The thermal decomposition of diazirines in the gas phase is a homogeneous, first-order, and probably unimolecular process.[78,87-89] The Arrhenius parameters for the thermal decomposition of diazirines are shown in Table IV. The product ratios obtained during the pyrolysis studies differ from those obtained during the photolysis studies;[86,87,89] this difference supports the hypothesis that vibrationally excited carbene is produced in the photochemical decomposition. A theoretical investigation of the thermal destruction of diazirine has been published[90] in which some significant mechanistic details emerge. One of them is that the CH_2 produced during the pyrolysis is more likely a ${}^1A_1$ than a ${}^1\Delta_g$ state.

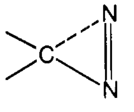
Liu and Toriyama[92] have discussed the nature of the pathway of ring rupture in the thermolysis of diazirines. They analyzed the three proposed activated complexes: **25a** proposed by Frey



25a



25b



25c

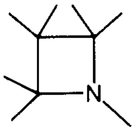
and Liu[89] for the thermal decomposition, which would be similar to that formed in step 2 of the photolytic rupture and give rise to a nonvibrationally excited carbene; **25b** proposed by Schmitz[93] for the liquid-phase thermolysis of some diazirines; and **25c** proposed by Liu and Toriyama[92] based on the arguments of Mitsch and co-workers[88,94] that the linear diazomethane is an intermediate prior to the loss of N_2. Liu and Toriyama[92] disregarded activated complex **25b** because of the small solvent effect they found in liquid-phase studies,[92,95,96] as well as the effect of substituents on the reaction rate. The substituent effect on the reaction rate also gave evidence against activated complex **25a**. Likewise in the gas-phase thermolysis, Liu and Toriyama[92] favored a homolytic stepwide rupture (intermediate **25c**). However, in a further study[97] on 3-methyl-3-vinyldiazirine the small solvent effect could not be used as an argument against activated complex **25b**, and the investigators were not certain whether the intermediate was of a diradical or ionic nature.

III. Four-Atom Rings

A. One Heteroatom

1. Nitrogen Compounds

There is no systematic study on either the thermal or the photolytic gas-phase behavior of the azetines **26** or of the azetidines **27**



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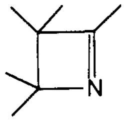

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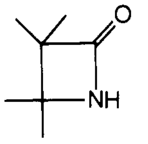

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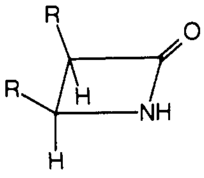
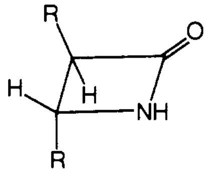


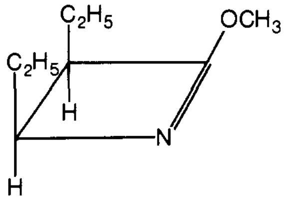
28a, R = CH_3
c, R = CH_3CH_2



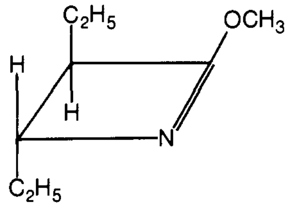
28b, R = CH_3
d, R = CH_3CH_2

TABLE V. Percentage Distribution of the Products from the Thermolysis of β-Lactams (from Paquette et al.[98])

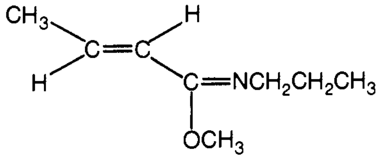
Starting lactam	*cis*-Butene-2	*trans*-Butene-2	*cis*-Hexene-3	*trans*-Hexene-3
28a	99.3	0.7		
28b	0.4	99.6		
28c			98.8	1.2
28d			0.5	99.5



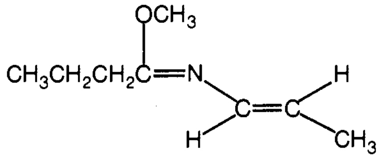
29a



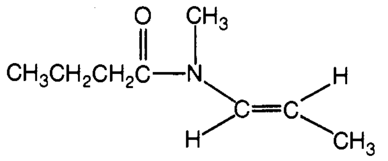
29b



30



31

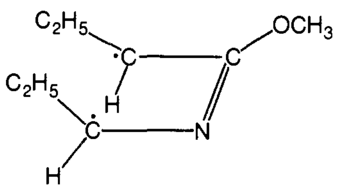


32

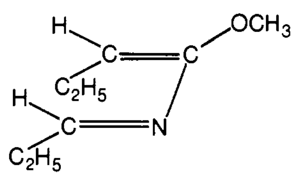
Paquette et al.[98] studied the thermal gas-phase fragmentation of β-lactams **28** in a N_2 stream with different substituents on the carbon atoms and compared it with the pyrolysis of 1-azetines. The β-lactams studied were **28a–d**. The four β-lactams were stable up to 500 °C. At 600 °C the yield of fragmentation was larger than 90%, giving an alkene and cyanuric acid as products. Table V shows the percentage distribution of the products. The results show that the thermal fragmentation of the β-lactams proceeded with total retention of stereo configuration. This would indicate a concerted process involving the simultaneous rupture of two ring bonds instead of a single bond fission leading to a biradical. When the vapor-phase pyrolysis of **29a** and **29b** was studied at 600 °C in N_2 at 23 Torr pressure of the compound, the products found were **30–32**. The proportion of the three compounds was as follows:

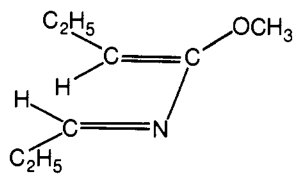
	Products at 600 °C, %		
Compound pyrolyzed	30	31	32
29a	14	78	8
29b	12	77	11

At 700 °C, **32** predominated at the expense of **31** for both compounds **29a** and **29b**. The investigators suggested that the products could be explained equally well by two different mechanisms, one involving a C–C fission giving rise to the following biradical



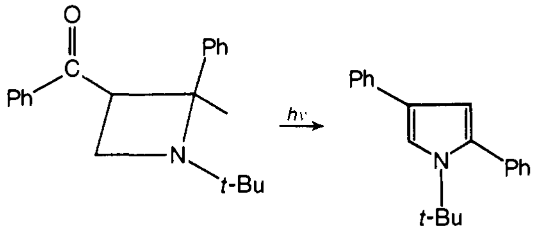
and the other involving conrotatory opening of the ring to give rise to the following two intermediates, respectively, followed





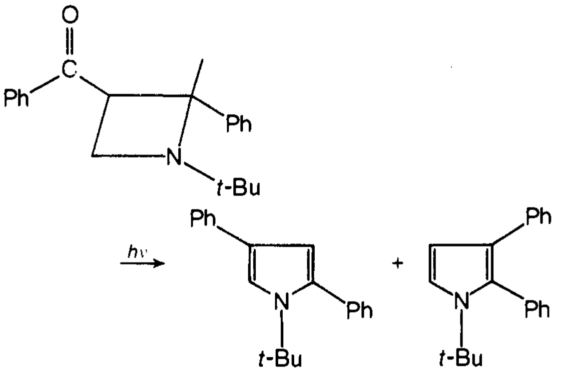
by allylic H shifts. The results obtained from the β-lactam pyrolyses when compared with those from the azetine pyrolyses imply that the β-lactams have available a reaction path inaccessible to the azetines. Much more work is needed in the gas-phase thermolysis and photolysis of these compounds.

It is worth mentioning a ring expansion reaction occurring in liquid phase for *cis*-*N*-*tert*-butyl-2-phenyl-3-benzoylazetidine reported by Padwa and co-workers[99] which bears a relation with our further discussion on the five-membered rings. This was said to be the first example of a photochemical migration of an alkyl group from the α position to the carbonyl carbon of an (n → π^*) excited state. The compound was dissolved in ethanol and irradiated with λ >300 nm. See reaction 50a. The photorearrangement could not be quenched by triplet quenchers, leading the investigators to speculate about two possibilities: either the rearrangement of the (n → π^*) triplet is too rapid for diffusion of the excited species to collide with the quencher molecules, or the reaction proceeded from a singlet state. It was not possible for the investigators to decide between these two possibilities.



(50a)

Reaction 50a was substantiated in later work,[100] but it was shown that the reaction is substantially altered for the trans isomer. Irradiation of the trans isomer gave a mixture of 2,3- and 2,4-diphenyl-*N*-*tert*-butylpyrroles with the 2,3 isomer being formed about twice as frequently as the 2,4 isomer. Sensitization and emission studies[101] indicated that both reactions 50a and 50b are derived from the lowest triplet state. The failure to quench implies that the reactions are too rapid for the diffusion of the excited state to the quencher molecule.

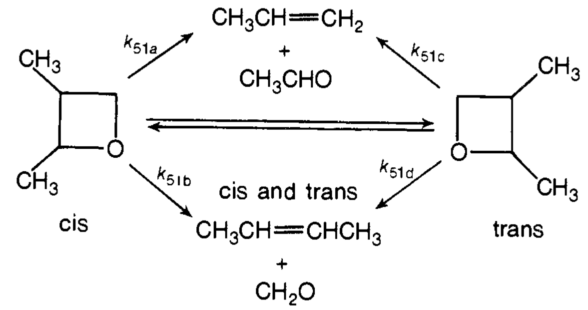


(50b)

2. Oxygen Compounds

Although oxetanes are important compounds as intermediates in the oxidation of hydrocarbons,[102] few fundamental studies about their photochemical and thermal behavior have been conducted. Bittker and Walters[103] first studied the gas-phase thermal decomposition of trimethylene oxide (oxetane) between 54 and 330 Torr in a temperature range between 420 and 460 °C with and without added NO, C_3H_6, and toluene. The reaction rate was about 10% slower in the presence of the free radical scavengers. In the presence of these scavengers, it was found that the decomposition was homogeneous and first order giving rise to C_2H_4 and CH_2O as primary products, with an activation energy of 60 kcal/mol and a preexponential factor of 6.1 × 10^{14} s^{-1} for the temperature range studied. The investigation yielded no information which could distinguish between a concerted or biradical mechanism. Cohoe and Walters[104] studied the thermal decomposition of 3,3-dimethyloxetane between 400 and 450 °C at 10 Torr pressure and again a homogeneous first-order split into two smaller molecules was found, giving rise to an olefin (isobutene in this case) and CH_2O. The determined activation energy was 60.7 kcal/mol with a preexponential factor of 3.8 × 10^{15} s^{-1}, and they were unaffected by the addition of the free radical scavengers NO or C_3H_6 to the reaction mixture. The investigators pointed out that if a biradical mechanism is involved, the biradical must decompose rapidly. From their data they could not decide whether the C–C bond or the C–O bond would be the first to be broken. Slightly higher Arrhenius parameters were found by Holbrook and Scott[105] who reported a preexponential factor of 5.2 × 10^{15} s^{-1} and an activation energy of 63.0 kcal/mol between 420 and 480 °C. They extended the study to low pressures to observe the falloff in rate coefficient and found the half-pressure to be 1 Torr at 464.4 °C.

SCHEME III



The thermal decompositions of 3-ethyl-3-methyloxetane and 3,3-diethyloxetane were studied by Clements et al.[106] Both decompositions were first-order homogeneous molecular eliminations which the investigators felt probably proceeded through a biradical intermediate. The former compound was studied at 407–488 °C; the products were 2-methyl-1-butene and CH_2O, with $\log(k/s^{-1}) = 15.357 \pm 0.151 - (60045 \pm 482)/\theta$. The latter compound was studied at 402–463 °C; the products were 2-ethyl-1-butene and CH_2O, with $\log(k/s^{-1}) = 15.297 \pm 0.063 - (59716 \pm 200)/\theta$.

O'Neal and Benson[107] estimated the activation energies and the preexponential factors for dissociations and isomerizations (structural and geometric) of three- and four-membered cyclic compounds including the cyclic ethers. Thermodynamic estimates of the transition state parameters were made in terms of a biradical mechanism, and excellent agreement between the observed and calculated Arrhenius parameters was found. In particular, for oxetane the calculated E_A was 59 kcal/mol and $\log A = 14.7$. The corresponding observed values were 60 kcal/mol and 14.78.[103]

Holbrook and Scott[108] very recently again raised the question of the biradical mechanism vs. a concerted molecular split in their study of the pyrolyses of *cis*- and *trans*-2,3-dimethyloxetane. The pressures used were between 2 and 32 Torr and the temperature between 415 and 483 °C. The products formed in reactions 51a–d were followed (Scheme III), and the corresponding rate expressions were obtained:

$$\log(k_{51a}/s^{-1}) = (15.70 \pm 0.22) - (63216 \pm 621)/4.576T$$

$$\log(k_{51b}/s^{-1}) = (15.24 \pm 0.25) - (62493 \pm 715)/4.576T$$

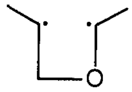
$$\log(k_{51c}/s^{-1}) = (15.91 \pm 0.25) - (64652 \pm 644)/4.576T$$

$$\log(k_{51d}/s^{-1}) = (15.49 \pm 0.26) - (63676 \pm 745)/4.576T$$

It was observed that the cis–trans isomerization of the oxetane itself was relatively unimportant and that the pyrolyses were unaffected by addition of NO. It was also observed that there was a partial retention of configuration; i.e., the *cis*-oxetane gave 68% *cis*-butene, and the *trans*-oxetane gave 76% *trans*-butene.

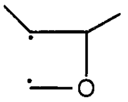
All of these observations suggest a direct molecular split. Nevertheless the magnitude of the *A* factors of the reaction rate coefficients and the resulting calculated $\Delta S^{\dagger}$ were consistent with processes involving ring opening through a biradical, and this path was favored by Holbrook and Scott.[108] The possible explanation for the partial retention of configuration upon decomposition was that the 1,4 biradical intermediate was capable of existing for only very few rotations before decomposition. Since decomposition was much faster than isomerization, it was postulated that the biradical once formed decomposed much faster than it rotated about its bonds.

The question of which bond was cleaved to produce the biradical was still unanswered, and four possible biradicals were considered (**33a–d**).



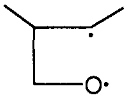
$\longrightarrow C_3H_6 + CH_3CHO$ (52)

33a



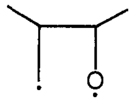
$\longrightarrow C_4H_8 + CH_2O$ (53)

33b



$\longrightarrow C_4H_8 + CH_2O$ (54)

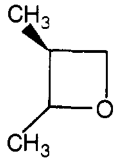
33c



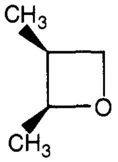
$\longrightarrow C_3H_6 + CH_3CHO$ (55)

33d

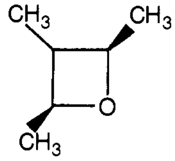
The two possible bond fissions (C–C and C–O) were again considered by Carless[109] to explain the results obtained during the gas-phase pyrolyses of seven different substituted oxetanes. The compounds studied were **34a–g**. The mole ratios of alkenes produced are listed in Table VI. The partial retention of configuration found from the decomposition of compounds **34a** and **34b** was the same (within the experimental error) as found by Holbrook and Scott.[108] Carless found 74% *trans*-butene from *trans*-2,3-dimethyloxetane (**34a**) and 64% *cis*-butene from the *cis*-oxetane (**34b**). In this work two biradicals were also proposed (one from C–C cleavage and the other from C–O cleavage). The results obtained by Carless[109] were in contrast with those reported by Jones and Staires[110] who observed higher stereoselectivity during pyrolysis of *cis*- and *trans*-2-methyl-3-phenyloxetane at 410–470 °C, particularly for the trans isomer which retained configuration 95% of the time. The high stereoselectivity in this case may reflect restricted rotations of the biradical due to the large phenyl group.



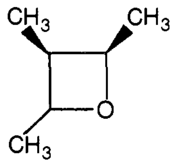
34a



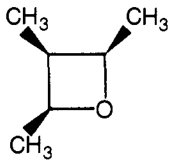
34b



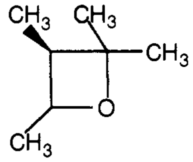
34c



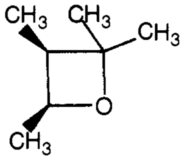
34d



34e

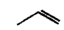
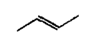
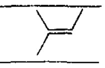


34f



34g

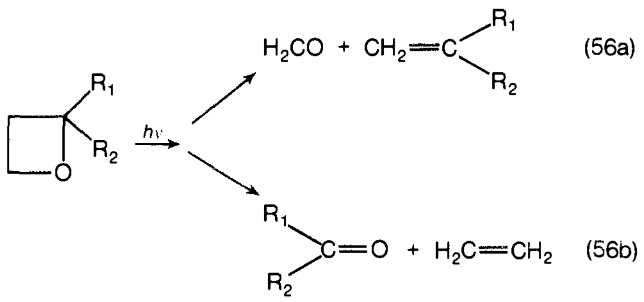
TABLE VI. Mole Ratios of Olefin Produced in the Thermal Decomposition of Methyl-Substituted Oxetanes[a]

Oxetane pyrolyzed	Olefin produced (mole ratio)			
				
34a	4.55	2.85	1.00	
34b	3.25	0.55	1.00	
34c		3.05	1.00	
34d		1.30	1.00	
34e		0.36	1.00	
34f		2.30	1.00	60
34g		0.62	1.00	22

[a] From Carless.[109]

Most of the evidence indicates that the thermal decomposition proceeds through a biradical which may decompose before undergoing rotation. This interpretation is favored on theoretical grounds also, since the direct molecular split would violate the Woodward–Hoffmann orbital symmetry rules.

The only photochemical study of oxetanes in the gas phase, to our knowledge, was performed by Margerum et al.[111] Oxetane itself and the 2,2-dimethyl derivative were irradiated in the gas phase at room temperature with a mercury arc (effective wavelengths: 200.2, 197.3, and 194.2 nm). For oxetane a temperature study (25–154 °C) was also conducted. 2-Phenyloxetane was also studied, but in isooctane solution. Processes 56a and 56b accounted for 98% of the products. For 2-phenyloxetane probably reaction 56a was favored over reaction 56b. For the dimethyloxetanes both splits were almost equally important.

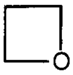


$H_2CO + CH_2{=}C(R_1)R_2$ (56a)

$R_1R_2C{=}O + H_2C{=}CH_2$ (56b)

The biradical mechanism could explain the results obtained during this study. In an attempt to trap the biradical, oxetane was also photolyzed in solution and as a solid at −196 °C. No evidence was found for the existence of a stable biradical. Thus if a biradical is involved, it would be highly energetic and decompose immediately. It should be pointed out that in the photodecomposition, the concerted molecular split to products is allowed by the orbital symmetry rules.

A wavelength study would be very interesting in this case, for comparison with the results obtained with the oxirane molecule since Margerum et al.[111] found that the three processes 57a–c,



$\longrightarrow CH_3 + CH_2CHO$ (57a)

$\longrightarrow C_2H_5 + HCO$ (57b)

$\longrightarrow CH_3CH_2CHO$ (57c)

equivalent to those postulated for oxirane,[18] were unimportant in this case. It would be important also to study both the thermal and photochemical behavior of the same oxetane to be able to determine a mechanism for its decomposition upon excitation with different amounts of energy.

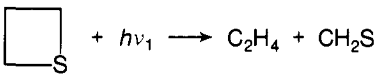
Above 120 °C, the oxetane photolysis gave as additional products H_2, CO, CH_4, and C_2H_6. These were attributed to free radical attack, the free radicals coming from the secondary photolysis of CH_2O.[111] That these products are produced from free radical attack on oxetane was shown by preparing CH_3 radicals from acetone photolysis at 120–154 °C in the presence of oxetane and observing these products.

3. Sulfur Compounds

The thietane molecule and some of its derivatives have been the object of several gas-phase studies during the last few years. Wiebe and Heicklen[112] excited the thietane molecule by four different means. Radiation at 213.9, 228.8, and 253.7 nm and mercury sensitization at 253.7 nm were used. Experiments were performed at different temperatures, pressures, and light intensities in the absence and presence of several foreign gases. In all cases the products were C_2H_4, C_3H_6 (cyclopropane and propylene), and polymer. No new products were formed upon addition of *i*-C_4H_8, thus indicating the absence of S atoms. Since the ultraviolet absorption spectrum of thietane vapor consists of two different regions, one extending from 300 to 230 nm and a much stronger one extending from 230 to 206 nm, it seems reasonable that with the different wavelengths used, different electronic and vibrational levels of the excited molecule should be involved.

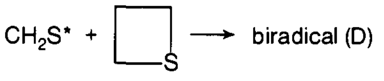
In order to account for the results obtained, especially the C_3H_6 yields, the investigators postulated the intervention of several intermediates in the mechanism. When 253.7-nm radiation was used, the electronic state should have been the same as the one involved in the experiments of Dice and Steer[113] who used 254- and 313-nm radiation. These investigators found that the only primary products were ethylene and thioformaldehyde, and that the small amount of propylene was in fact produced by a secondary photolysis of the thioformaldehyde formed.

The mechanism proposed by Wiebe and Heicklen[112] to account for the C_3 products was



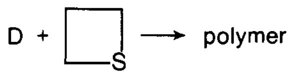
(58)

$$CH_2S + h\nu_2 \longrightarrow CH_2S^* \quad (59)$$



(60)

$$D \longrightarrow C_3H_6 + CH_2S_2 \quad (61)$$

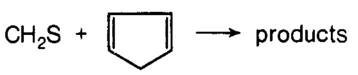


(62)

It was found that only part of the propylene production was quenched by NO, and this part was attributed to the decomposition of the biradical D whose nature could not be established. The lifetime of D was estimated to be greater than 1.2 × 10^{-5} s at 205 °C.

The nature of the intermediate species produced when thietanes are excited within their long wavelength absorption bands was elucidated by Dice and Steer[114,115] in further studies on *cis*- and *trans*-3-ethyl-2-propylthietane. In the earlier study on thietane[113] it was found that the addition of common radical trapping agents did not have any effect on the yields of the two primary products C_2H_4 and CH_2S. However, it was not possible to clearly distinguish between a molecular pathway or a single bond cleavage as the primary step. In the study of the photolysis of *cis*- and *trans*-3-ethyl-2-propylthietane at 200 °C with λ 313 nm, it was again found that neither the addition of NO nor CO_2 had any effect on the product yield.[115] However, the fact that both *cis*- and *trans*-hept-3-ene isomers together with isomerized substrate were found as products was a clear indication that initial cleavage of the C–S bond and subsequent rotation around the C–C bond were taking place. All the evidence in this study was in favor of an almost exclusive biradical mechanism. This initially formed biradical was postulated to be very short lived (like the one postulated for oxetane[109]) decomposing to olefin and the thioaldehyde before any scavenging could occur. The rapid decomposition occurred before equilibration of the biradical intermediate, and the ratio of *cis*-3-heptene to *trans*-3-heptene was not the same when starting with the *cis*- and *trans*-thietanes even in the presence of 1 atm of CO_2.[114,115] On the other hand, in the Hg(6^3P) sensitized photodecomposition of 3-ethyl-2-propylthietane vapor, the cis/trans product ratios at high pressures of Ar were the same from either the cis or trans starting material.[115] This indicated that the biradical in the Hg-photosensitized studies was longer lived and could be equilibrated before decomposition.

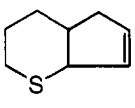
The production of monomeric thioformaldehyde during the photolysis of thietane with 313-nm radiation was confirmed by Dice and Steer[116] by adding cyclopentadiene to the cyclic sulfide and finding, after photolysis of the mixture, the corresponding 1,4 Diels–Alder cycloaddition product of thioformaldehyde to cyclopentadiene. The product found was 2-thiabicyclo[2.2.1]-hept-5-ene. The rate constant for the reaction



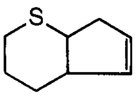
(63)

was found to be $k_{63} \simeq 2 \times 10^2$ M^{-1} s^{-1} at 200 °C.

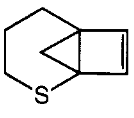
Another product (or products) found in small yield had a molecular weight of 140, and the investigators could not distinguish between possibilities **35, 36,** and **37,** but it confirmed the pres-



35

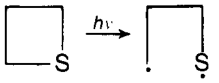


36



37

ence of a biradical initially formed through reaction 64, which

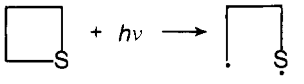


(64)

in turn added to cyclopentadiene or decomposed to C_2H_4 and CH_2S, or even added to another thietane molecule to produce dithiooctane in very small yields.

In a more recent paper, Dice and Steer[117] presented a complete study and discussion of the mechanism of thietane and some derivative photolyses in the vapor phase, solution, and glassy matrices. The products obtained upon thermal decomposition of thietane at 250 °C were also reported in this paper. There were considerable amounts of a nonvolatile yellow oil and small amounts of H_2S, C_2H_4, C_2H_6, C_3H_6, and C_3H_8.

Three means of photochemically exciting the thietane compounds were used by Dice and Steer:[117] radiation at 313 and 290 nm and Hg sensitization at 253.7 nm. The previous proposal of a biradical intermediate was confirmed for the lowest lying singlet state. The mechanism included reactions 64–70. Re-



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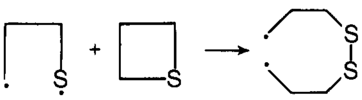

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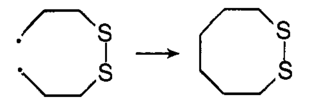
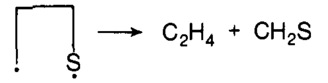
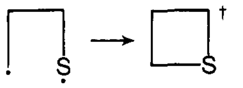
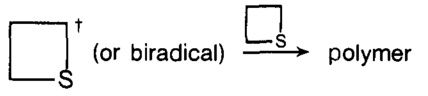

(66)

1,2-dithiocane (DTO)



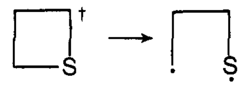
(67a)


(67b)



(68)

i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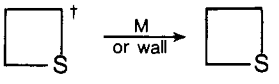
ii



(70)

action 64 was found to be the only primary process. Since it was found that only at high temperatures $\Phi\{C_2H_4\} + \Phi\{DTO\}$ approached 1 for incident radiation at 313 nm, it seemed reasonable to postulate a ring closure reaction 67b which, in addition, was confirmed when the photolysis of 3-ethyl-2-propylthietane (EPT) was analyzed. In this last case the isomerized substrate was found, thus indicating that reaction 67b was operative. The ring closure reaction was found to be less efficient in the unsubstituted thietane than in the substituted ones.

In regard to the temperature effect on the ethylene quantum yield, Wiebe and Heicklen[112] found that with 253.7-nm incident radiation there was little temperature dependence, $\Phi\{C_2H_4\} > 0.80$ even at 25 °C. However, with 313.0-nm incident radiation Dice and Steer[117] found $\Phi\{C_2H_4\}$ to be only 0.48 at 25 °C.

It was thought by Dice and Steer that reaction 68 or 70 was the most likely fate of i (see reaction 68). In particular i could be vibrationally excited ground state thietane responsible for the polymer formation in a way analogous to the one occurring during thermolysis of the compound.

The biradical formed in reaction 69 was not necessarily the same as the one formed in the primary process and could undergo different subsequent reactions. Further evidence for biradical ii (reaction 69) was found when the liquid-phase or solid-state studies were performed.[117] It was claimed that the biradical was actually trapped and its spectrum taken in glassy matrices. Speculation was made about the nature of the biradical formed in reaction 64, and it was assumed that the upper state of thietane was unbound giving rise to a biradical in its singlet state. The same was postulated by Wiebe and Heicklen.[112]

During Hg sensitization triplet-state thietane should be produced. However, triplet-state species did not seem to be involved in the direct photolysis,[112,117] indicating that the intersystem crossing of singlet thietane to triplet thietane is a negligible process.

The only study performed on the gas-phase photolysis of thietane within its second absorption band (230 to 206 nm) was the one by Wiebe and Heicklen.[112] The products were the same as in the long wavelength region (C_2H_4, c-C_3H_6, C_3H_6, and polymer) though in different relative yields. The relative ratio $\Phi\{C_3\}/\Phi\{C_2\}$ markedly increased with the energy of the incident radiation (228.8 or 213.9 nm). To explain the results, four excited states and an intermediate different from the one produced at 253.7 nm were proposed. It was noticed that the intermediate could be of a biradical nature. The nature of the excited states was not clear and more experimental data are needed in the high-energy absorption band.

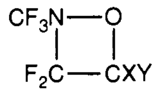
Trimethylene sulfone, $\overline{CH_2CH_2CH_2SO_2}$, has been flash thermolyzed by King et al.[118] At 950 °C the products were C_3H_6, c-C_3H_6, and SO_2. At 365–405 °C, Cornell and Tsang[119] found only equal amounts of c-C_3H_6 and SO_2, the rate coefficient expression for decomposition being $k = 10^{16.1\pm0.3} \exp\{-55835 \pm 994)/RT\}$ s^{-1}.

Block et al.[126] have studied the flash vapor pyrolysis at 300–500 °C of trimethylene sulfone and have identified sulfine CH_2SO as a product.

B. Two Heteroatoms

1. Oxazetidines

The only gas-phase studies of oxazetidines were performed by Banks et al.[120] on the photolytic decomposition of some 1,2-oxazetidines (**38** and **39**), with X and Y being different halo substituents: F, Cl, or CF_3; and by Barr and Haszeldine[121] and Barr et al.[122] on the thermal decomposition of compounds like **38**.



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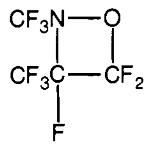
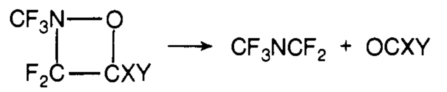


39

The pyrolysis of compounds of type **38** at 550 °C was found to follow reaction 71. The photolysis of these compounds follow essentially the same pattern.



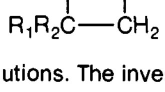
(71)

The mechanism postulated was a cleavage of the N–O and of the C–C bonds although there is no evidence in favor of the two possible alternatives: biradical or concerted mechanism. However, in the light of all the available evidence so far accumulated, it is possible to assert that all the four-membered ring decompositions occur primarily through initial biradical formation.

2. Dioxetanes

The very interesting 1,2-dioxetanes have been studied in solution by Kopecky and Mumford.[123] These compounds are unique because they produce excited carbonyl molecules which luminesce upon thermal decomposition even in benzene solution at 60 °C.

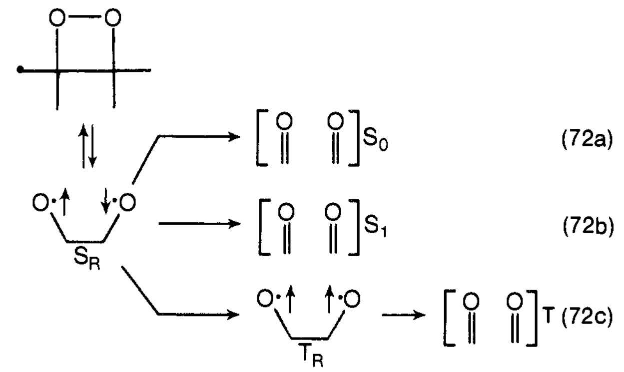
Richardson et al.[124] studied the kinetics of the thermal decomposition of 3,3-diphenyl- and 3,3-dibenzyl-1,2-dioxetane in



benzene and CCl_4 solutions. The investigators concluded from the study that here again a two-step mechanism was operative in which the rate-determining step was the ring opening giving rise to the corresponding biradical in a singlet state (Scheme IV). The singlet biradical (S_R) could then decompose into the carbonyl compounds in either their ground singlet state or in an excited singlet state, or could undergo intersystem crossing to a triplet state (T_R), which in turn could decompose to the carbonyl compounds in their triplet state.

In an interesting review on the different aspects of the chemistry of 1,2-dioxetanes in liquid phase,[125] this mechanism was again favored. The review especially emphasized the decomposition of tetramethyl-1,2-dioxetane. It was pointed out that

SCHEME IV



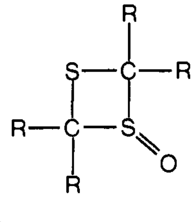
electronically excited carbonyl compounds can be produced because of the high energy content of dioxetanes. This high energy content is the result of the strain energy of a small ring compound, weakness of the O–O bond linkage, and the potential for a huge energy release upon the formation of two carbonyl groups. With tetramethyl-1,2-dioxetane, electronically excited singlet acetone is produced in 0.5% of the decompositions and triplet acetone is produced in 50% of the decompositions as determined by reaction with *trans*-dicyanoethylene. Also both the fluorescence and phosphorescence of acetone are easily detected.

The preference for triplet formation is a strong violation of the spin conservation rules and indicates that reaction 72c is the favored pathway. This spin conservation violation was attributed by Turro et al.[125] to electron spin-electron orbital coupling because of the change in orbitals of the p electrons on the oxygen atom. Of even more fundamental importance is why electronically excited state formation is so important. This can be understood in terms of the Woodward–Hoffmann rules which show that the production of two ground-state acetone molecules is forbidden by orbital symmetry considerations.

Another interesting effect discussed by Turro et al.[125] is that the triplet acetone produced can sensitize the decomposition of tetramethyl-1,2-dioxetane which regenerates the triplet acetone. The chain length of this process can reach 1000 in CH_3CN solution. Thus the decomposition is autocatalytic.

3. 1,3-Dithietane 1-Oxides

In the flash vapor photolysis of 1,3-dithietane 1-oxides at ~400 °C, Block et al.[126] found the corresponding sulfine CR_2SO and CR_2S as products.



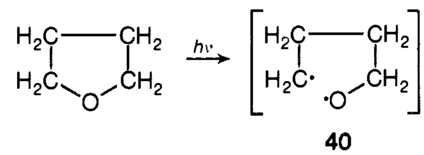
R = H or CH_3

IV. Five-Atom Rings

A. One Heteroatom

1. Saturated Compounds

Oxolane. The gas-phase photolysis of tetrahydrofuran (oxolane) was studied by Roquitte[127] who extended his earlier preliminary report.[128] The later study was done between 30 and 120 °C using from 10 to 165 Torr of reactant and radiation of $\lambda < 220$ nm. Since a medium-pressure mercury arc was used, the effective wavelengths were 197.3 and 194.2 nm. The major products of decomposition were CO, H_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, c-C_3H_6, and CH_2O together with other minor products (C_4H_{10}, butene-2, and butadiene). The mechanism postulated included the formation of an excited biradical (**40**) by cleavage

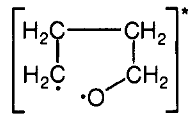


(73)

40

of the C–O bond. Since the excitation used was 145 kcal/mol and the C–O bond dissociation energy is of the order of 84.1 to 85.2 kcal/mol,[129] the initially formed biradical was expected to be highly excited and decompose to a variety of products.

Steps 74a–d were proposed to account for the formation of



$$\longrightarrow \cdot CH_2CH_2\dot{C}H_2{}^* + CH_2O \qquad (74a)$$

$$\longrightarrow C_2H_4 + CH_3 + H + CO \qquad (74b)$$

$$\xrightarrow{(+M)} C_3H_8 + CO \qquad (74c)$$

the observed products. Reaction 74c was considered to be partially enhanced by raising the pressure since the relative CO yield increased and the relative CH_2O and C_2H_4 yields decreased as the pressure was raised. (Quantitative data on the C_3H_8 yields were not obtained.) However, the relative CH_2O and C_2H_4 yields did not drop toward zero but reached some limiting values, thus indicating that reactions 74a and 74b were only partially supressed by raising the pressure.

The cyclopropane yield increased with pressure to an upper limiting value, but it did not equal the limiting value of the CH_2O yield. Thus the following steps were needed to account for the cyclopropane pressure dependence

$$\dot{C}H_2CH_2\dot{C}H_2{}^* \rightarrow C_3H_6 \qquad (75a)$$

$$\rightarrow c\text{-}C_3H_6{}^* \qquad (75b)$$

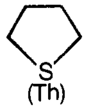
$$c\text{-}C_3H_6{}^* \rightarrow C_3H_6 \qquad (76)$$

$$c\text{-}C_3H_6{}^* + M \rightarrow c\text{-}C_3H_6 + M \qquad (77)$$

The existence of the trimethylene diradical was supported by previous evidence.[130] From the measured yields of cyclopropane as a function of pressure, the excess energy carried by the cyclopropane was estimated to be in the range 79–86 kcal/mol from an RRKM calculation. Since the total excess energy of the reaction was 115 kcal/mol, the remaining 29–36 kcal/mol might excite other products in the system. The calculated energy content of the cyclopropane formed appeared to be significantly less than the one obtained during the photolysis of ketene in the presence of ethylene. The calculated average lifetime of the excited cyclopropane was of the order of 10^{-7} s, which was in accord with the value obtained during the thermal isomerization of cyclopropane at 445 °C.[131]

Thiolane. The photolysis of tetrahydrothiophene (thiolane) vapor was studied by Braslavsky and Heicklen[132] at room temperature with 213.9-nm radiation. The major product was C_2H_4; next in importance were 1-C_4H_8, C_3H_6, and C_2H_6; CH_4, c-C_3H_6, 1,3-C_4H_6, CH_2CHSH, c-CH_2CH_2S, and 1-C_4H_9SH were minor products. Traces of H_2, C_3H_8, *n*-C_4H_{10}, and c-C_4H_8 (cyclobutane) were also found. A polymer and a very unstable product tentatively identified as 1-butene-1-thiol were also detected. The ethylene quantum yield was pressure quenched. The other gas-phase products apparently were pressure independent, though the results were too scattered due to the low quantum yields to draw any definite conclusion.

At that time a two-excited-state mechanism was proposed to account for the different behavior of the different products toward pressure changes



(Th)

$$+\ h\nu \longrightarrow Th^* \qquad (78a)$$

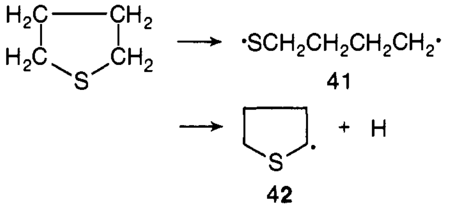
$$\longrightarrow Th^{**} \qquad (78b)$$

$$\mathrm{Th^*} \longrightarrow \mathrm{C_2H_4} + \cdot\mathrm{CH_2CH_2S}\cdot \qquad (79)$$

$$\mathrm{Th^*} + \mathrm{Th} \longrightarrow 2\mathrm{Th} \qquad (80)$$

where Th stands for thiolane. Th** would be the precursor of the other products found, either by decomposition into C_3 products or reaction with thiolane to give C_4 products and S_2.

Sulfur atoms were not found in the system, contrary to the results at 253.7 nm where $S(^3P)$ was found.[133] When thiolane was irradiated at 253.7 nm the products were 1-C_4H_9SH, 1-C_4H_8, C_3H_6, and c-C_3H_6, the latter two compounds being in the ratio 3.6 to 1. H_2, polymer, and equal amounts of C_2H_4 and c-CH_2CH_2S were also reported. The C_2 and C_3 products were of about equal importance. In principle two different routes were postulated to explain the results obtained in this case, involving two different radicals **41** and **42.** It could be that the two excited states postulated by Braslavsky and Heicklen[132] preceded the formation of the two radicals **41** and **42** postulated by Sidhu,[133] the difference in incident wavelength being responsible for the different proportion of the products. More experimental data are needed on this system to elucidate the mechanism of photodecomposition, though there seems to be important differences between the behavior of oxolane and that of thiolane. One of the reasons for the observed differences could be that Roquitte[127] studied the oxolane photolyses at much higher pressures than those used by Braslavsky and Heicklen,[132] thus quenching the decomposition of some of the excited species.



(81a)

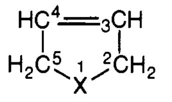
41

(81b)

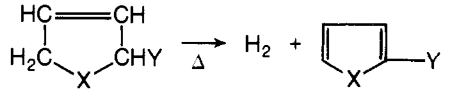
42

2. Monoolefins

The thermal decomposition of compounds of the general type



with X = CH_2, O, CH═CH, NH, or S has been discussed by Wellington et al.[134] Heating all of these compounds eliminates H_2, giving rise to the corresponding aromatic heterocyclic compound. Thus a general mechanism was postulated involving a transition state in which the 2- and 5-hydrogen atoms were brought into sufficient proximity to interact. An analogous transition state was proposed previously for the decomposition of cyclohexa-1,4-diene.[135] The general equation would be



(82)

Wellington et al.[134] measured the rate constant for the thermal decomposition of the thiophene derivative 2,5-dihydrothiophene and found a homogeneous, first-order reaction. In this case, as in the other studies with X = CH_2,[136,137] X = O,[138] X = CH═CH,[135,139] and X = NH,[140] the ratio between the aromatic heterocycle and H_2 was 1:1, but in the 2,5-dihydrothiophene case H_2S was also found, the amount of which corresponded to about 30% of the thiophene produced. Polymer was found in this last case, as well as in the 3-pyrroline case.[140]

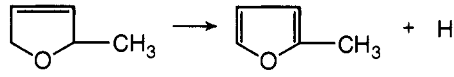
Wellington et al.[134] tabulated the Arrhenius parameters, and they are listed in Table VII. They correlated the kinetic and molecular parameters for the decomposition reaction and postulated that the driving force of the reaction was the resonance energy of the product formed in each case. An important role in determining the activation energy was played by the H(2)–H(5) distance. A series of assumptions was made, for instance, that all the 2,5-dihydro compounds except 3-pyrroline were planar molecules. (This conformation had been experimentally determined for the 2,5-dihydrofuran case by Beach.[142]) The correlation found between the experimentally determined activation energies for the reaction (with due allowance for the difference in resonance energies between reactant and product) and the H(2)–H(5) distance was very good. The only anomalous cases, the 2,5-dihydrofuran and its methyl derivative, were explained by considering that the high electronegativity of the O atom could facilitate the formation of the transition state.

TABLE VII. Arrhenius Parameters for the Thermal H_2 Elimination of Five-Membered Ring Heterocycle Compounds of the Type $\overline{\mathrm{CH_2CH{=}CHCHYX}}$

X	Y	$10^{12}A$, s^{-1}	E_a, kcal/mol	Temp range, °C	Ref
NH	H	1.9 ± 0.4	44.6 ± 0.241	317–358	140
CH═CH	H	1.05	42.69	303–343	135
CH═CH	H	2.4 ± 0.7	43.8 ± 0.4	330–390	139
CH_2	H	11.0	58.8	483–548	136
O	H	5.3 ± 0.1	48.5	342–409	138
O	Me	6.77 ± 0.25	48.33 ± 0.05	342–420	141
S	H	17[a]	54.8 ± 3.5		134

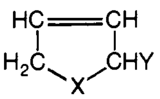
[a] Factor of 4 uncertainty.

Additional support for this mechanism was the small negative entropy of activation (−3.2 eu) found, for instance, in the 2-methyl-2,5-dihydrofuran decomposition[141] which supported the suggestion of a rigid transition state. In this last system the reaction was again found to be first order and homogeneous with a rate coefficient of $(6.77 \pm 0.25) \times 10^{12} \exp\{(-48330 \pm 50)/RT\}\ s^{-1}$ for the decomposition (reaction 83). In none of these gas-phase pyrolyses of the 2,5-dihydro heterocyclic five-membered compounds did NO have any effect on the product yields, leading to the conclusion that chain or free-radical reactions were absent.

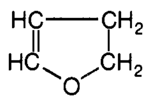


(83)

Contrary to the case of compounds of type **43** which decompose by eliminating molecular H_2, the isomeric compound **44** decomposes only at more elevated temperatures by chain scission above 375 °C to give cyclopropanecarboxaldehyde, and by a free-radical mechanism to give CO and C_3H_6.[143] Crotonaldehyde was also found. As the temperature increased the product distribution favored CO plus C_3H_6, and at 550 °C these were practically the only products. The reason for the difference between the isomeric forms is that compound **43** conserves orbital symmetry and obeys the Woodward–Hoffmann rules during a cis elimination of H_2, whereas compound **44** does not.



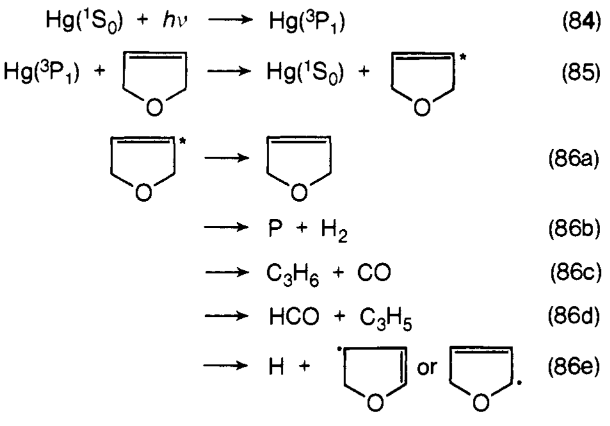
43



44

The photochemistry of monoolefinic heterocyclic compounds has been studied only for the furan derivatives. Francis and Sherwood[144] studied the mercury-sensitized decomposition of 2,5-dihydrofuran using pressures from 10 to 15 Torr at 25 ± 2 °C. The main products found were H_2, CO, and C_3H_6, with smaller amounts of allene, biallyl, furan, 2,3-dihydrofuran, and tetrahydrofuran. Three less volatile products difficult to identify were also found. For extended radiations a nonvolatile product was formed. The mechanism proposed is given in Scheme V. The measured quantum yields were: for reaction 86b, 23%; for reaction 86c + 86d, 43%; and for reaction 86e, 34%.

SCHEME V



NO addition confirmed that radicals produced some of the products but did not change the quantum yield of CO or H_2, thus indicating that these two products came from an intramolecular rearrangement of the initially formed excited state. Since the quantum yield of H_2 was much larger than that for furan in the absence of NO, the investigators concluded that the product P of reaction 86b was not furan, but a reactive species instead. The investigators did not consider other sources of H_2.

The biradical $\cdot OCH_2CH{=}CH\dot{C}H_2$ was considered as a possible precursor for some of the products found. However, since during the study of the addition of O(^{3}P) to butadiene,[145] no five-membered ring was found among the products, it was concluded that either electron delocalization might not be complete enough to make the intermediates in both cases identical, or that a concerted mechanism without an identifiable biradical was operative. It could be that the birdical had a short enough lifetime to decompose prior to recyclization, as was the case in the three- and four-membered rings.

Schmidt and Roquitte[146] in a preliminary report on the photochemistry of 2,5-dihydrofuran claimed CO and C_3H_6 to be the only major products; no H_2 was found.

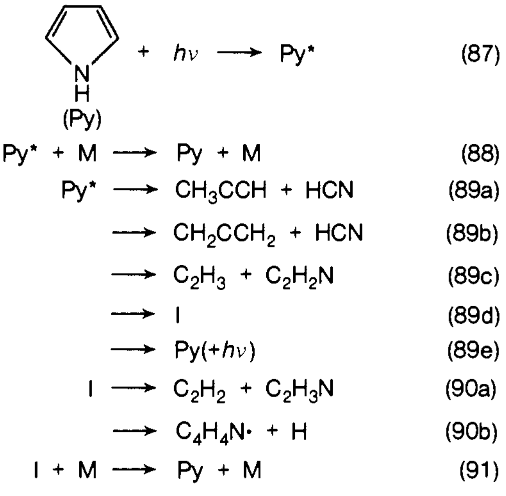
The experimental evidence tends to point to a decomposition behavior of the dihydrofuran molecule dependent on the type of excitation energy. For the 2,5-dihydrofuran (compound type **43**) thermal excitation gives rise to furan and H_2; Hg($^3P_1$) sensitization gives rise to several processes, two of them being excited or reactive furan + H_2 and C_3H_6 + CO; and excitation to within a singlet band produces C_3H_6 + CO. Presumably in the electronically excited state, the molecular orbital symmetry is changed, Woodward–Hoffmann rules do not permit the cis elimination of molecular H_2, and decomposition is by a free-radical process. During Hg sensitization a triplet state is formed and many processes may occur. This idea is supported by the fact that the thermal decomposition of 2,3-dihydrofuran (compound **44**) proceeds exclusively by the free-radical route. We would predict that photochemical decomposition would give rise to the elimination of molecular H_2, though this experiment has not been done yet.

The biradical mechanism in the decomposition of the 2,5-dihydrothiophene derivatives was favored by Kellogg and Prins[147] from their liquid-phase studies, for photochemical excitation as well as for thermal initiation.

3. Diolefins

All of the five-membered diolefin heterocycles possess a conjugated diene ring, somewhat modified by the presence of the different heteroatom, which gives them an aromatic-like stability. The pyrrolic compounds are the least aromatic of the family, the aromaticity increasing in the following order: pyrrole < furan < thiophene < benzene. Tellurophene and selenophene (the nonsaturated five-membered rings with Te and Se, respectively, as the heteroatom) are located between furan and thiophene in this scale.[148]

SCHEME VI



A review of the chemistry of the five-membered ring aromatic heterocyclic compounds has been given by Lablache-Combier and Remy.[149] This review which is in French deals mainly with the solution-phase reactions.

Pyrroles. Wu and Heicklen[150] studied the photolysis of 0.05 to 4.7 Torr of pyrrole vapor at 213.9 nm and room temperature. The main products were CH_3CCH (methylacetylene), CH_2CCH_2 (allene), C_2H_4, H_2, and C_2H_2. Minor products were CH_4 and C_3H_6, which were secondary products resulting from the reaction of H atoms with the C_3H_4 products. N_2 and C_2N_2 were not found, but HCN and polymer were. The mechanism outlined to explain the results included the reactions in Scheme VI together with other secondary processes to account for the observed products. HCN was difficult to analyze and was not quantitatively followed. NO and O_2 did not inhibit allene or CH_3CCH formation; therefore these products were postulated to come from a nonradical singlet species. On the other hand, NO and O_2 did inhibit C_2H_4 formation giving experimental evidence for reaction 89c. Reaction 89e was postulated to account for the low total quantum yield even at zero pressure, although no emission for this compound has so far been reported in the gas phase.

I was an intermediate of an undefined nature. It could not be a triplet state because C_2H_2 formation was not repressed by adding NO or O_2, and it could not be a ring-contracted intermediate because it would then have given C_3 compounds. Besides H_2 production through H atoms produced in reaction 90b, molecular production of H_2 was postulated to account for the fact that its production was not completely inhibited by radical scavengers. Mullen and Orloff[151] had studied the UV absorption spectrum of pyrrole and found that there are two bands, one below 217 nm and a low-intensity broad shoulder between 223 and 250 nm. They assigned this shoulder to the $\pi \rightarrow \pi^*$ transition, and it could be that under the conditions used by Wu and Heicklen,[150] both singlet states were present, one of them being the intermediate I. This last hypothesis could be elucidated by performing photochemical studies at several different wavelengths.

The postulated radical $C_4H_4N\cdot$ could be the one previously detected during flash photolysis studies of pyrrole by Callear and Lee.[152]

In a further study on the photolyses of methyl derivatives of pyrrole, Wu and Heicklen[153] investigated the 2,5- and 2,4-dimethylpyrrole vapor photochemistry at room temperature using from 0.05 to 0.70 Torr of the reactants. This time two wavelengths were used: 213.9 and 228.8 nm. The only products found were H_2, CH_4, C_2H_6, and polymer. No products coming from ring cleavage were detected, this leading the authors to postulate that CH_3 substitution stabilizes the ring, thus inhibiting its decomposition. The mechanism proposed was

$$\mathrm{DMP} + h\nu \rightarrow \mathrm{DMP}^* \qquad (92)$$

$$\mathrm{DMP}^* \rightarrow \mathrm{H} + \mathrm{F_a} \qquad (93a)$$

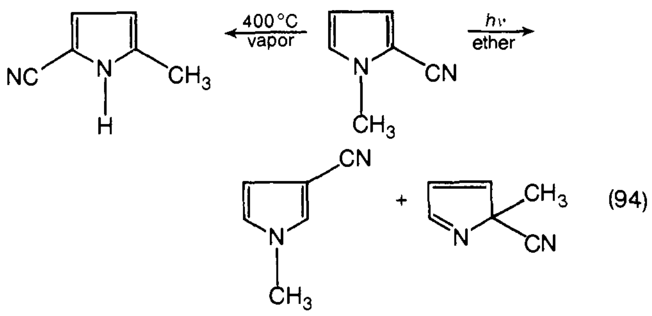
$$\rightarrow CH_3 + \mathrm{F_b} \qquad (93b)$$

$$\rightarrow \mathrm{DMP} \qquad (93c)$$

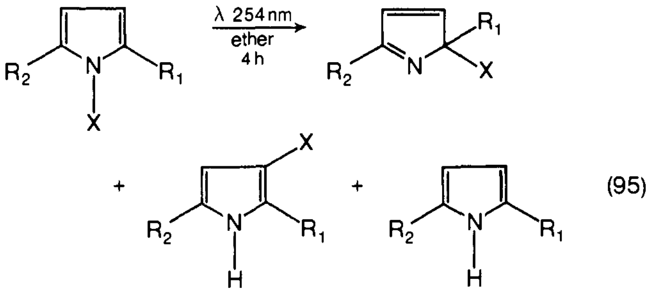
where DMP means dimethylpyrrole and F_a and F_b are fragments of a radical nature.

Unfortunately the isomerization of the photolyzed pyrroles could not be followed, because of analytical problems, and no evidence could be found regarding the importance of CH_3 migration during photolyses. Earlier work in solution has shown that substituted pyrroles undergo only valence isomerization. Thus the thermal[154] and photochemical[155] 1 ↔ 2 and 1 ↔ 3 isomerizations of N-substituted pyrroles have been reported. However, it was shown that the 2 isomer was not the precursor of the 3 isomer in the photochemical reaction of *N*-benzylpyrrole because the 2 isomer did not photoisomerize to the 3 isomer, though it did so interconvert thermally. On the other hand, Hiraoka[156] found that the irradiation of 2-cyanopyrrole in methanol yielded the 3 isomer as a major product, but the reaction was not reversible.

Comparing the thermal and photochemical behavior of some pyrrole derivatives, Hiraoka[157] concluded that in the *N*-methyl-2-cyanopyrrole case the thermal and photochemical reactions originated from different states. Equation 94 accounts for Hiraoka's findings.

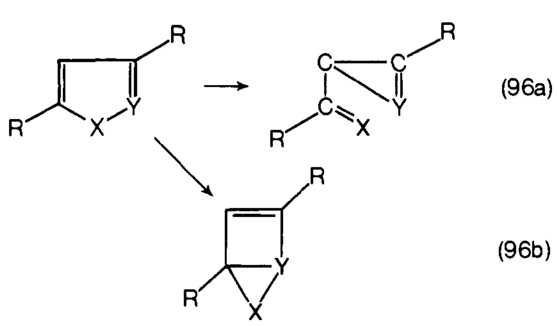


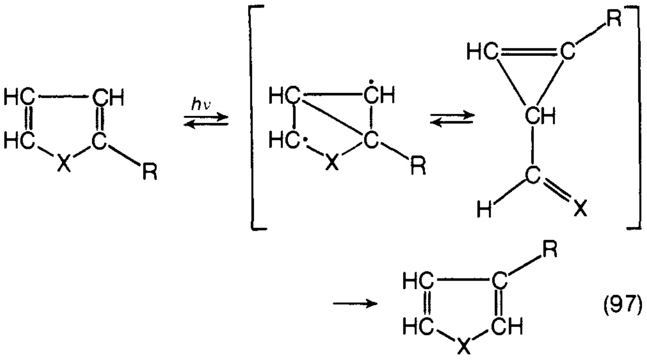
These results agree with Patterson and co-workers'[158] later results on the photoisomerization of (N-substituted allyl) dialkylpyrroles in ether. The latter investigators found that substitution in positions 2 and 5 of the pyrrole ring did not inhibit 1 to 3 migration; instead the overall conversion was improved. Reaction 95 held. They also found some ring cleavage and determined that the cleavage paralleled the isomerization, i.e., that cleavage and isomerization were competitive processes from the same excited intermediate.



Because of the importance of pyrrolic derivatives in clinical chemistry, much work has been done in the photochemistry and photooxidation of these compounds in solution. A brief review has been published recently on the subject.[159]

The photoisomerization of many of the five-membered aromatic heterocyclic compounds can be related to the main paths 96a and 96b. It is worth noting that neither of these two kinds of derivatives has been isolated from pyrrolic compounds photochemically, although the ring-contracted compound could be thought as an intermediate in the 2 ↔ 3 isomerization (eq 97).

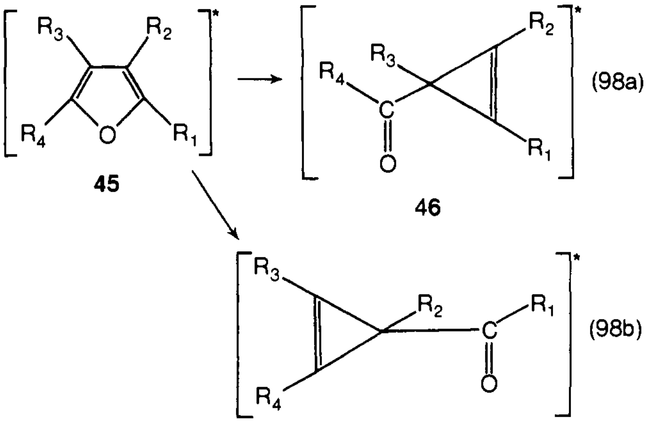




However, this mechanism leaves open the question of the nonexisting 3 ↔ 2 isomerization[155,156] in some pyrroles.

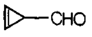
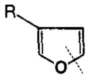
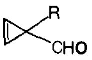
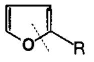
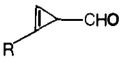
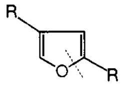
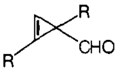
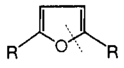
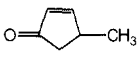
Furans. An intensive study of the photochemical and thermal behavior of the furanic derivatives has been undertaken by Hiraoka, Srinivasan, and co-workers, analyzing the reactions in the gas phase and in solution. The main purpose of all the research done has been to elucidate the nature of the intermediates involved. The Hg($^3P_1$) sensitized photolysis of furan itself,[160-162] several alkyl derivatives,[163-165] cyano derivatives,[166,167] and furfural[168] were investigated.

The general conclusion from these studies was that after excitation the furanic molecule underwent a bond cleavage between the O and α-C giving rise immediately to ring-contracted excited species (reactions 98a and 98b). These two excited species could, in turn, get deactivated, lose CO giving rise to isomeric linear or cyclic C_4 compounds, or rearrange to give some other furanic derivatives. The excited species **45** would be a triplet if it is produced by Hg($^3P_1$) sensitization; the pressure dependence of many of the products found with furan[160-162] itself and its derivatives[165] supports triplet production. The intermediacy of cyclopropenyl carbonyl compounds **46** and **47** has been proved experimentally several times. van Tamelen and Whitesides[169] isolated these kind of compounds while studying



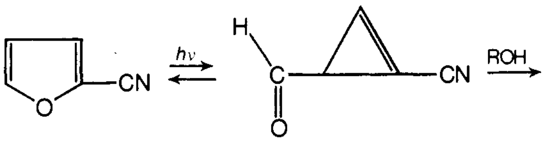
45 **46** **47**

TABLE VIII. Hg (6^3P_1) Sensitized Photolysis of Furans[a]

Furan and most important bond cleavage	R	Proposed intermediate
		
	CH_3, CN	
	CH_3, CN, CHO, CH=CH_2	
	CH_3	
	CH_3	

[a] From Srinivasan.[170]

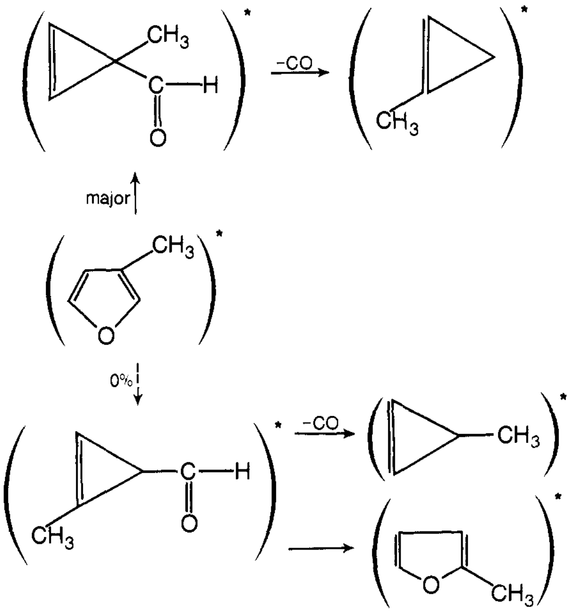
the photodecomposition of 2,5-di-*tert*-butyl, 2,4-di-*tert*-butyl- and 2,3,5-tri-*tert*-butylfurans in solution. Hiraoka[167] reported finding 1-alkoxy-2-cyanocyclopropane-3-carboxaldehydes when 2-cyanofuran was photolyzed in alcoholic solution, giving further evidence for the formation of the ring contracted aldehyde. The reaction would be as follows:



cyclopropanecarboxaldehydes (99)

One of the most interesting features of the ring contraction undergone by the furanic derivatives when it is Hg($^3P_1$) sensitized is the selectivity of the contraction. The bond broken depends largely on the position of the ring substituent.[170] The general results are summarized in Table VIII.

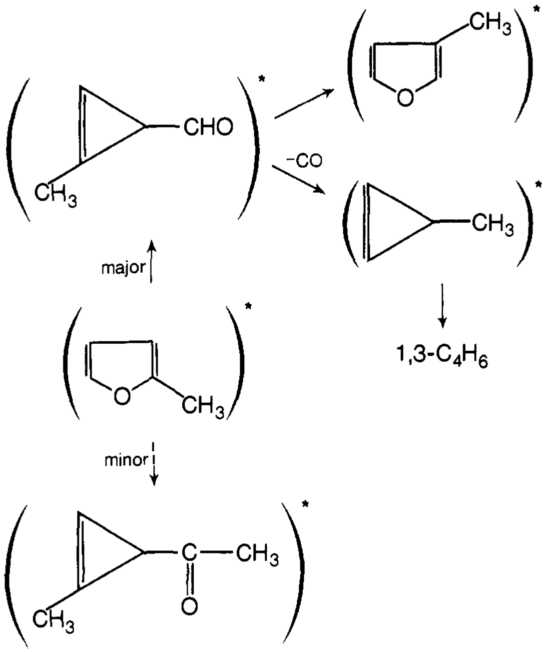
Hiraoka[164] reported that 3-methylfuran isomerized to 3-methylcyclopropene-3-carboxyaldehyde and yielded 1-methylcyclopropene with no trace of 3-methylcyclopropene (reactions 100a and 100b) derived from the alternative transient 1-methylcyclopropene-3-carboxyaldehyde. In the vapor phase direct photolysis of 3-methylfuran,[164] the selective ring contraction to 3-methylcyclopropene-3-carboxaldehyde disappeared and the ring contraction to 1-methylcyclopropene-3-carboxaldehyde (reaction 100b) also occurred giving 2-methylfuran and 3-methylcyclopropene upon decarbonylation. The loss of selectivity was explained by assuming a partial contribution of a second excited state, upon direct irradiation, in which the bond O–C_2 is the weakest one.



(100a)

(100b)

The major reaction path of 2-methylfuran, instead, appeared to be isomerization to 1-methylcyclopropene-3-carboxaldehyde by either direct or Hg(6^3P_1) sensitized photolysis, which then gave 3-methylcyclopropene and 1,3-C_4H_6 as major products[161,163,164] (eq 101–c). In addition to 3-methylfurn and CO, also found were methylacetylene, 1,2-C_4H_6, and 1-C_4H_6.[164]

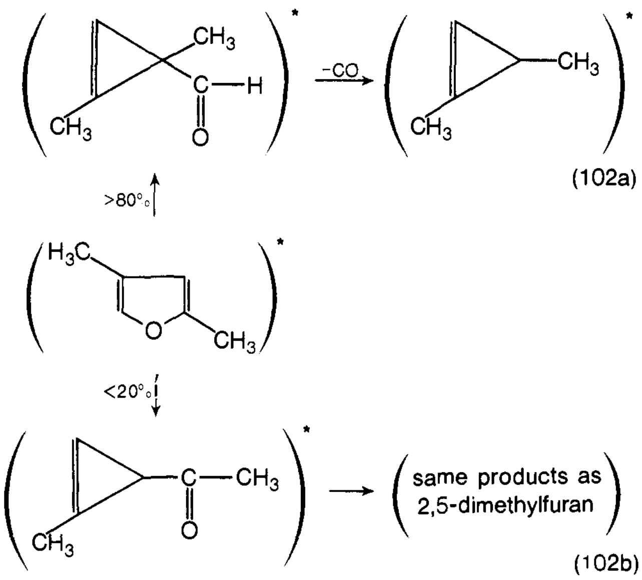


(101a)

(101b)

(101c)

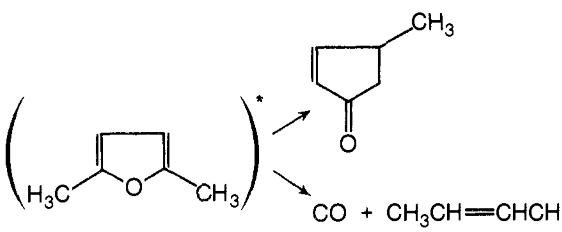
The principal reaction of 2,4-dimethylfuran was the isomerization to 1,3-dimethylcyclopropene-3-carboxaldehyde.[164] This decomposed predominantly to 1,3-dimethylcyclopropene and CO, giving rise to products different from the ones for 2,5-dimethylfuran[165] (eq 102a,b).



(102a)

(102b)

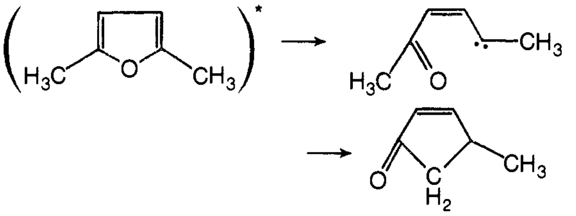
While direct irradiation of 2,5-dimethylfuran in the vapor phase gave some 2,4-dimethylfuran among the products,[163] when 2,5-dimethylfuran was photosensitized[165] 4-methylcyclopent-2-en-1-one, 1,3-pentadiene, and CO were found as major products. The chemical reactions of the excited molecule were



(103a)

(103b)

thought to be reactions 103a and 103b. The photoisomerization reaction 103a was a very novel reaction and was claimed to be intramolecular because there was no O_2 quenching effect. The investigators explained it by postulating a carbene intermediate which internally inserts into a C–H bond in the CH_3 group across the C bearing the two unbonded electrons (eq 104).



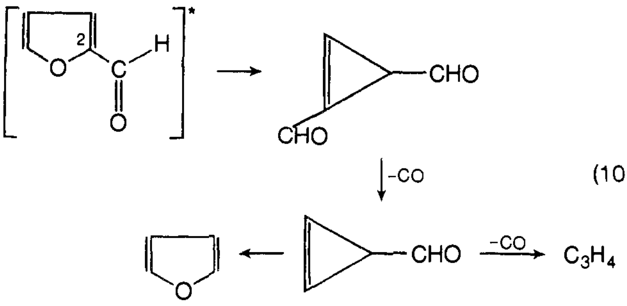
(104)

In previous work by Srinivasan[161] on furan itself, carbenes were postulated as possible intermediates to account for the Diels–Alder adducts that were seen with dienes, but in that case the carbene pathway was a minor one compared with the ring contraction pathway. In 2,5-dimethylfuran the situation seemed to be reversed. This strong influence of substituents on the reaction paths for the substituted furans still deserves more work.

The explanation for this experimentally determined high selectivity was found in the strength of the bond to be broken prior to the formation of the ring-contracted carboxaldehyde. Hiraoka[164] calculated the π bond orders of the furans using the simple Hückel molecular orbital model for ground and lowest excited states, understanding by lowest excited state an average of the lowest singlet and triplet states. In order to determine the bond strength, the σ bond order had to be added to the calculated π bond order. The ring contraction would then start with the fission of the weakest bond in the lowest excited state, that is, the bond of lowest order. It was found that all the experimental results so far obtained were compatible with the breakage of the predicted weakest bond of the excited state. The initial step was the production of a short-lived biradical, by fission of the weakest bond, as was the case in all the other heterocyclic compounds so far analyzed.

Studies have been made with groups other than the methyl group as the ring substituent. Thus with formyl, vinyl, or cyano as the ring substituent, the results are similar.

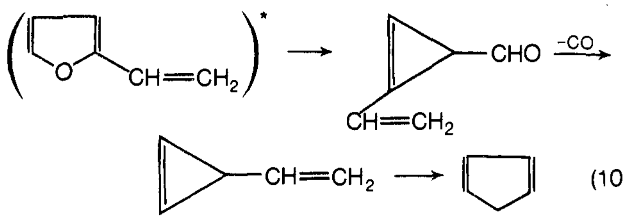
The Hg($^3P_1$) sensitization and the direct photolysis at 3130–2225 Å of 2-furfuraldehyde[168] resulted in the production of furan, C_3H_4 compounds, and CO as major products (eq 105).



(105)

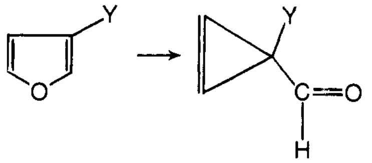
Cyclopropene was found among the C_3H_4 products only in the Hg(6^3P_1) sensitized studies and not in the direct irradiations, suggesting that a triplet excited state is necessary to produce cyclopropene. Here again Hiraoka[164] explained the results by use of the bond-order method, which leads to the conclusion that the C_2–O bond is the weakest.

The Hg($^3P_1$) sensitization of 2-vinylfuran gave cyclopentadiene as one of the principal products, suggesting to Hiraoka[164] the mechanism of eq 106.



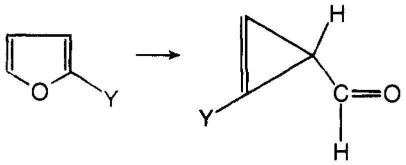
(106)

When the cyano-substituted furans were studied, it was confirmed that the 3-substituted furans give 3-substituted cyclopropenecarboxaldehyde (reaction 107), whereas the 2-



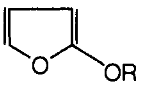
(107)

substituted furans yield 1-substituted cyclopropene-3-carboxaldehyde (reaction 108).[166,167] These results are in agreement with the previous findings and calculations.[164]



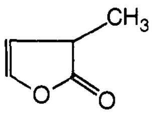
(108)

On the other hand, the photolysis, both directly and by Hg sensitization, is quite different for compounds of type **48**. Sri-

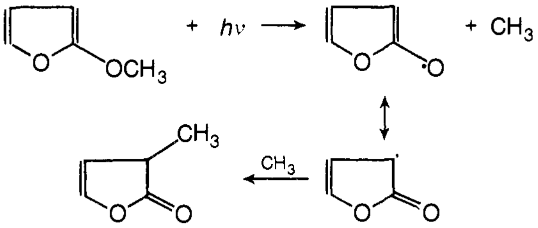


48, R = CH_3, CH_3CO

nivasan and Hiraoka[171] found that the exclusive ring product with R = CH_3 was

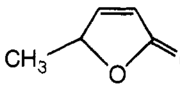


Also produced was C_2H_6. It along with the above lactone was eliminated in the presence of O_2 suggesting an entirely free-radical mechanism 109. The photochemistry of **48** with R =



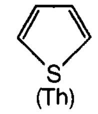
(109)

CH_3CO is quite complex. The products include furan, acetic acid, and



The mechanism of the reaction is not clear but the investigators favored a free-radical process.

Thiophenes. The photochemical reactions of thiophene in the gas phase were studied by Wiebe and Heicklen.[172] Radiation of 213.9 and 228.8 nm was used, as well as mercury sensitization at 253.7 nm. Experiments were done at three temperatures: 25, 200, and 305 °C, and at various pressures and light intensities as well as in the presence of different foreign gases. In all cases the products were C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, and CH_2HCCCH. Polymer was also found. The mechanism postulated to account for the experimental results included the initial formation of the vibrationally excited, lowest excited singlet state, designated Th* (eq 110). The transition involved when the molecule was directly excited was said to be π, π^*.



(Th)

$$+ h\nu \longrightarrow \mathrm{Th}^* \qquad (110)$$

The quenching and decomposition steps included were the following:

$$\mathrm{Th}^* + \mathrm{M} \rightarrow \mathrm{Th} + \mathrm{M} \qquad (111)$$

$$\mathrm{Th}^* \rightarrow \mathrm{I}^* \qquad (112a)$$

$$\rightarrow \mathrm{Th} + h\nu \qquad (112b)$$

$$\rightarrow C_2H_2 + C_2H_2S \qquad (112c)$$

$$\rightarrow \cdot\mathrm{CHCHCHCHS}\cdot \qquad (112d)$$

$$\rightarrow CH_3CCH + CS^* \qquad (112e)$$

Reactions 111 and 112b might lead to triplet states and reaction 112a was needed to explain a pressure effect on the ratio of quantum yields of two of the products analyzed: CH_2CCH_2 and C_2H_2. The investigators said that the intermediate I might be the so-called valene intermediate suggested in the studies on arylthiophenes in the liquid phase.[173] Presumably it was not the triplet state, which should be scavenged by O_2 (which was not found), nor the ring-contracted intermediate similar to the one postulated for the furans, which should lead to cyclopropene. It must be said that propyne, which could come from hot cyclopropene, was found.

The addition of olefins did not produce episulfides, indicating that S atoms were not produced in the system. In reaction 112d, a long-lived biradical was postulated as an intermediate. The addition of O_2 drastically reduced the yield of two of the products, CS_2 and CH_2CHCCH. This effect was explained by assuming quenching of the CS and ·CHCHCHCHS· species by O_2:

$$O_2 + CS \rightarrow COS + O \qquad (113)$$

$$O_2 + \cdot\mathrm{CHCHCHCHS}\cdot \rightarrow SO_2 + CH_2CHCCH \qquad (114)$$

Also the C_2H_2S produced in reaction 112c was thought to be removed by O_2 as in the reaction

$$O_2 + C_2H_2S \rightarrow SO_2 + C_2H_2 \qquad (115)$$

The structure of the C_2H_2S species was envisioned as c-CH=CHS by analogy with some previous results of Strausz et al.[49] who found the same kind of intermediate while photolyzing c-CH=CHN=NS and who ruled out the $CH_2{=}C{=}S$ structure from spectroscopic evidence.

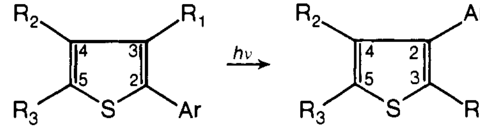
The results obtained by Wiebe and Heicklen[172] were fitted fairly well by their kinetic scheme, and several rate constants were determined. As part of their mechanism the investigators had to include the following step

$$\mathrm{I}^* \rightarrow \mathrm{B}^* \qquad (116)$$

assigning to B a triplet nature because of the scavenging effect by O_2.

Since the results obtained using direct irradiation and $Hg(^3P_1)$ sensitization were the same, the same mechanism was used to explain them. This brings up the question of the multiplicity of the excited state responsible for the production of products when direct irradiation was used. With the two sources of radiation, only minor differences were found, and they were explained just in terms of the difference of energy input between the direct radiation and the one transferred by the excited mercury atoms. To determine the nature of the excited states involved still requires more experimental results.

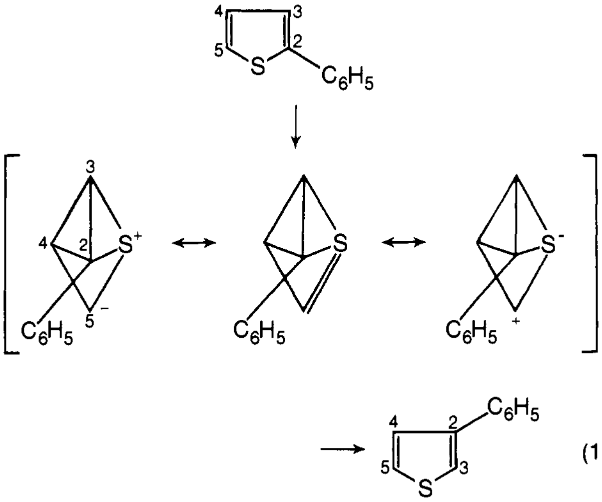
Wynberg and co-workers[173–178] studied the photolyses of substituted thiophenes in solution and observed a 2 → 3 shift of the substituents. Labeling experiments showed that the ring carbons actually moved carrying the substituent groups with them. The general equation would be the following



(117)

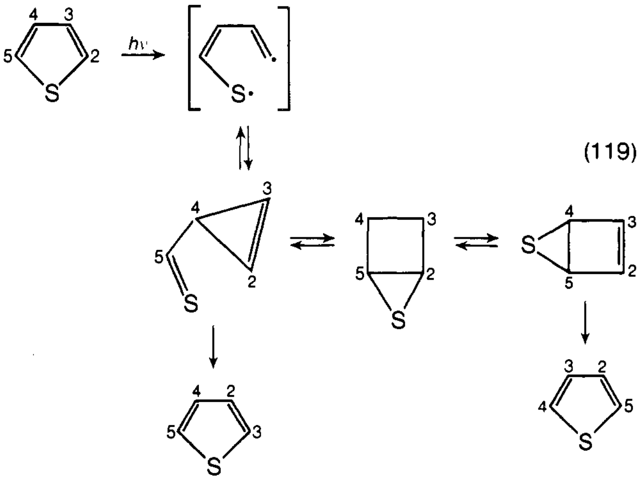
where Ar stands for an aromatic substituent.

No inversion of the C_4–C_5 atoms was found. After a complete analysis, the investigators explained their results obtained in the rearrangement by a valence-shell expansion of the sulfur atom (eq 118). They preferred charged intermediate species, especially because of the influence of polar media on the rate of rearrangement.



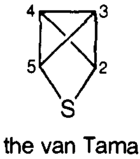
(118)

An alternative explanation was put forward by van Tamalen and Whitesides.[179] They proposed the scheme in eq 119 to account for the ring scrambling. However, Kellogg[180] pointed out this model does not account for C_3–C_4 interchange. He proposed that the excitation of the thiophene chromophore produced a drastic geometric distortion of the ring producing an

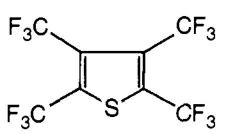


(119)

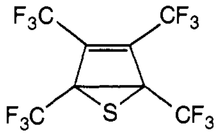
excited species in which three atoms remained in a plane and the other two were shifted 90° out of that plane. For different substituted thiophenes the pair of atoms shifted would be different depending upon the energy available to stabilize the excited state, which in turn depends on the influence of the substituents. The excited species would then either collapse to the starting material or rearrange to the products. According to Kellogg, the usual "turn over" would be of the C_2–C_3 bond. The intermediate would be the usual valence isomer



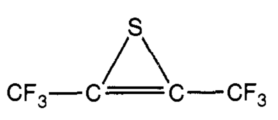
However, evidence for the van Tamalen–Whitesides proposal comes from the study of the liquid-phase photolysis of furanic and thiophenic compounds[181–183] in propylamine, where pyrroles were found in both cases. From the knowledge of the intermediacy of ring-contracted compounds in the furan case, the involvement of cyclopropenyl intermediates in the thiophene case was implied. Wiebe et al.[184] studied the gas-phase photolysis of tetra(trifluoromethyl)thiophene (**49**) in order to elucidate the nature of the intermediates in thiophene photolysis. The excitation used was either 213.9 nm or Hg($^3P_1$) sensitization. This compound was chosen since the migration of either CF_3 groups or fluorine atoms is not likely in the gas phase. The products of H migration in thiophene photolysis should be inhibited. The main gas-phase products found were hexafluorobutyne-2 and tetra(trifluoromethyl)cyclobutadiene episulfide (**50**). Two other minor gas phase products were detected. One of them was probably



49



50



and the other one was difficult to identify.

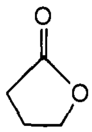
The isolation and characterization of **50** established the importance of valence bond intermediates (other than ring-contracted intermediates found in the photolysis of other five-membered heterocyclic compounds) in the photolysis of thiophenic compounds.

The mechanism proposed for 2-arylthiophenes failed to explain the results found with 3-arylthiophenes, where the 3 → 2 shift does not occur,[174] but all the other carbon atoms do scramble.[176] Furthermore, the question of the multiplicity and energy content of the excited species remained unanswered. It appeared that, in any case, the reaction involved the lowest (π,π^*) singlet state.

Furthermore, it is worth noting that carbonyl substitution appeared to inhibit the photoisomerization in thiophenes. This has been confirmed for the liquid-phase photolysis of benzoylthiophenes[185,186] where the main reaction these compounds underwent upon irradiation in solution was photocycloaddition to the carbonyl group.

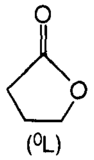
4. Lactones and Anhydrides

The photodecomposition of γ-butyrolactone (**51**) has been studied in the vapor phase[187] at 125 °C by excitation in three ways: direct 210.0–260.0 nm radiation, direct 253.7 nm, and Hg sensitization with 253.7 nm. When wavelengths from 210 to 260 nm were used, the products found were C_2H_4, CO, H_2CO, succinaldehyde, cyclopropane, propylene, and CO_2. Succinaldehyde and cyclopropane yields were independent of total pressure changes, while propylene and, to a lesser extent, the other products were pressure dependent. A complete mass balance was not achieved and this was attributed to polymer formation. When some experiments were conducted at longer wavelengths, as well as when Hg($^3P_1$) sensitization was used, the products found were the same. In the three cases, though, the product distribution changed. At longer wavelengths the formation of c-C_3H_6 and of C_3H_6 was favored. When Hg($^3P_1$) sensitization was used, C_2H_4 and succinaldehyde were less important than c-C_3H_6 and C_3H_6 as compared with the results obtained with 253.7 nm direct irradiation. Some thermal decomposition experiments showed that C_2H_4 was the major product, C_3 or succinaldehyde not being detected.



51

The mechanism proposed included two different triplet precursors for C_3H_6 and c-C_3H_6 since the sum of the two quantum yields did not remain constant. On the contrary, $\Phi\{C_3H_6\}$ was pressure dependent, whereas $\Phi\{\text{c-}C_3H_6\}$ was pressure independent. The mechanism proposed was:

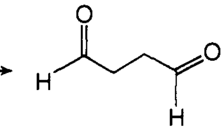


$$+\ h\nu \longrightarrow {}^1\text{L} \qquad (120)$$

(^{0}L)

$$^1\text{L} \longrightarrow {}^0\text{L}^\dagger \qquad (121a)$$

$$^1\text{L} \longrightarrow \qquad (121b)$$



succinaldehyde

$$^1\text{L} \rightarrow {}^3\text{L}' \qquad (121c)$$

$$^1\text{L} \rightarrow {}^3\text{L}'' \qquad (121d)$$

$$^0\text{L}^\dagger \rightarrow C_2H_4 + CO + CH_2O \qquad (122)$$

$$^0\text{L}^\dagger + M \rightarrow {}^0\text{L} + M \qquad (123)$$

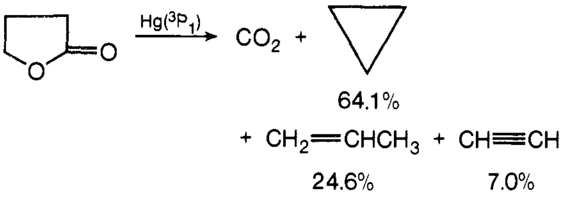
$$^0\text{L}' \rightarrow \text{c-}C_3H_6 + CO_2 \qquad (124)$$

$$^3\text{L}'' \rightarrow C_3H_6 + CO_2 \qquad (125)$$

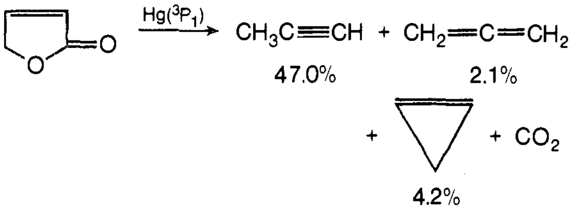
$$^3\text{L}'' + M \rightarrow {}^0\text{L} + M \qquad (126)$$

where L stands for butyrolactone, † represents vibrational excitation, and the superscripts 0, 1, and 3 stand for ground, singlet, and triplet, respectively. There are two different triplets ^{3}L′ and ^{3}L″. The butyrolactone, upon excitation, undergoes a n → π^* transition. However, below 200 nm a second very intense band appears which may overlap with the n → π^* transition in the 220–230-nm range. When λ = 253.7 nm was used, the transition would be $^1(n,\pi^*)$ exclusively, but when 210 to 260 nm radiation was used, two singlet states could be produced. The investigators postulated that when Hg($^3P_1$) sensitization was used, some singlet was being produced too. Since thermal decomposition gave exclusively C_2H_4, the authors favored the formation of some excited ground state during the photolysis, which in turn would give rise to C_2H_4 (reaction 122). Earlier work[188] had shown that the products of the liquid-phase photolysis of γ-butyrolactane at 253.7 nm gave succinaldehyde from a singlet state and cyclopropane (as well as allyl formate) from a triplet state.

In another study performed by Krull and Arnold[189] on the $Hg(^3P_1)$ sensitized decomposition of the same lactone (**51**) and of some other butenolides, the product distributions in eq 127–129 were found. No complete mechanism was given but



(127)



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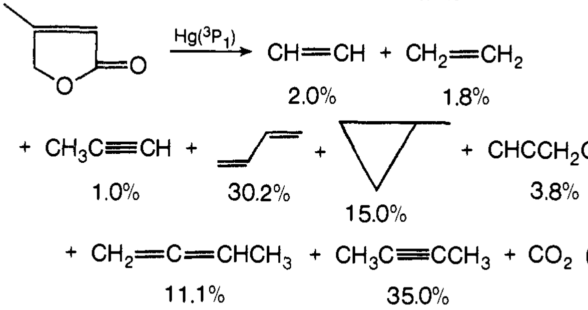
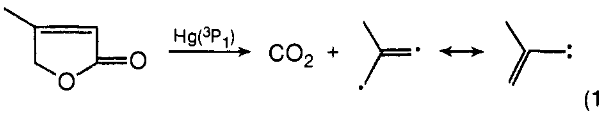


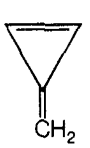
(129)

the initial step of eq 130 was postulated for the last compound.

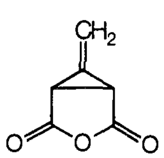


(130)

In an attempt to produce methylenecyclopropene (**52**), the gas-phase pyrolysis and the mercury-sensitized decomposition of *cis*-1-methylenecyclopropane-2,3-dicarboxylic anhydride (**53**)

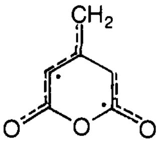


52

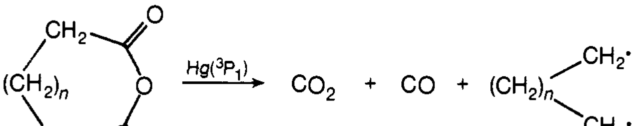


53

were performed.[190] The thermolysis at 720 °C gave the following products: $CH_2{=}CHC{\equiv}CH$ (46%), $CH{\equiv}CH$ (5%), $CH_3C{\equiv}CH$ (5%). No evidence for **52** was found. The $Hg(^3P_1)$ sensitization gave $CH_2{=}CHC{\equiv}CH$ (9%), $CH_3C{\equiv}CH$ (5%), $CH{\equiv}CH$ (5%), and polymeric material. An intermediate of the following kind was postulated.



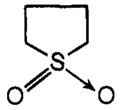
With cyclic lactones, the $Hg(^3P_1)$ sensitization gives rise to CO_2 and hydrocarbons; with cyclic anhydrides, it gives rise to both decarbonylation and decarboxylation. Krull and Arnold[191] found that the general reaction of cyclic anhydrides in the vapor phase is that given in eq 131. The radical in turn undergoes fragmentation, recycling, or H migration.



(131)

5. Sulfolanes

Honda et al.[192] studied the Hg and benzene photosensitization of sulfolane (**54a**). No products were formed with benzene



54a

photosensitization, but Hg(6^{3}P) sensitization at 70–130 °C gave as major products SO_2, C_2H_4, C_2H_2, and c-C_4H_8. Minor products were CH_4, C_2H_6, C_3H_8, and C_3H_6. The high-pressure limiting quantum yields of SO_2, c-C_4H_8, and C_2H_4 were 0.21, 0.04, and 0.17, respectively. From a study of the pressure effect of sulfolane and several quenching gases on the product ratios, the formation of energy-rich and thermal ethylene were deduced to be produced in equal amounts. The reaction scheme proposed was

$$Hg(^3P_1) + S(\text{sulfolane}) \rightarrow Hg(^1S_0) + {}^3S \qquad (132)$$

$$^3S \rightarrow \text{c-}C_4H_8 + SO_2 \qquad (133a)$$

$$\rightarrow C_2H_4^* + C_2H_4 + SO_2 \qquad (133b)$$

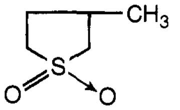
$$^3S(+M) \rightarrow S(+M) \qquad (134)$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \qquad (135)$$

$$C_2H_4^* + M \rightarrow C_2H_4 + M \qquad (136)$$

where ^3S is triplet sulfolane and $C_2H_4^*$ is energy-rich C_2H_4. By the use of deuterium-substituted sulfolane, it was established that C_2H_4 is produced by fission of the C_3–C_4 bond.

The pyrolysis of 3-methylsulfolane (**54b**) was studied at



54b

460–525 °C using a modification of the toluene flow method and a comparative rate technique.[119] The decomposition gave equal amounts of C_3H_6, C_2H_4, and SO_2 by a molecular route. The rate coefficient expression found was $k = 10^{16.1\pm0.4} \exp\{(-65\,970 \pm 1490)/RT\}\ s^{-1}$.

Other methyl-substituted sulfolanes were decomposed by Bezmenova et al.[193] At 500 °C they found the products to be SO_2 and the two corresponding substituted ethylenes.

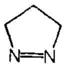
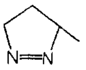
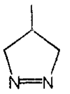
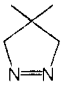
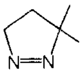
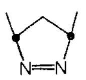
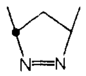
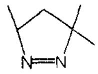
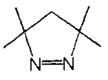
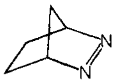
B. Two Heteroatoms

There is no report, to our knowledge, of the gas-phase thermolysis or photolysis of pyrazoles, imidazoles, oxazoles, isoxazoles, thiazoles, or their corresponding nonsaturated compounds. However, there is extensive literature on the pyrazolines and the dioxolanes.

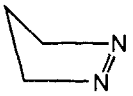
1. Pyrazolines

Pyrazoline is a five-membered ring with two adjacent nitrogen

TABLE IX. Rate Constants and Kinetic Parameters from the Pyrolysis of 1-Pyrazolines at 100–200 Torr (from Crawford and Mishra[194])

Compound	Temp range, °C	E_a, kcal mol^{-1}	Log A (s^{-1})	ΔS^{*}_{250}, eu
	202.0–237.3	42.4 ± 0.3	15.93 ± 0.13	11.2 ± 0.6
	190.5–230.0	41.0 ± 0.3	15.70 ± 0.15	10.1 ± 0.7
	199.5–234.5	42.2 ± 0.2	15.85 ± 0.05	10.8 ± 0.3
	247.5–286.1	42.8 ± 0.2	14.10 ± 0.07	2.9 ± 0.3
	184.2–211.4	40.0 ± 0.2	15.85 ± 0.03	10.8 ± 0.2
	191.0–224.0	40.3 ± 0.3	15.54 ± 0.11	9.4 ± 0.5
	181.0–220.3	40.2 ± 0.3	15.67 ± 0.11	10.0 ± 0.5
	183.6–215.1	39.0 ± 0.4	15.42 ± 0.21	8.4 ± 0.9
	176.6–219.3	37.7 ± 0.4	14.49 ± 0.12	4.6 ± 0.8
	171.0–202.4	36.9 ± 0.2 37.3 ± 0.3[a]	14.74 ± 0.10 14.90 ± 0.10[a]	5.8 ± 0.5 6.3 ± 0.5[a]

[a] From Cohen et al.[195]



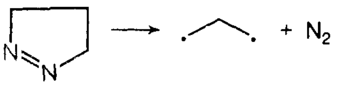
atoms. The Arrhenius parameters for the thermal decomposition of this compound and its methyl derivatives are given in Table IX.

As was reviewed by Strausz et al.[4] the thermolysis of pyrazoline and the alkyl- and alkenyl-substituted derivatives gives rise to N_2 and olefins or their isomeric cyclic hydrocarbon

$$\xrightarrow{\text{heat}} N_2 + C_3H_6 \text{ (or } \Delta) \qquad (137)$$

There are two main important interests in this reaction. One is the kind of intermediate produced in the initial step and the other is the energy distribution among the products of the reaction, which can also shed some light onto the problem of the intermediates involved.

The initial step of this general reaction was postulated by Crawford and co-workers[196] (and references therein) to be the simultaneous cleavage of both C–N bonds in a homolytic unimolecular process

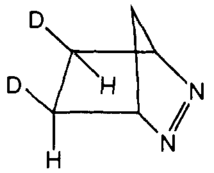


(138)

Al-Sadar and Crawford[197] found further evidence for the simultaneous double C–N bond cleavage mechanism and the production of the trimethylene biradical in measurements of the deuterium isotopic effect on the thermal decomposition rate coefficient.

However, McGreer et al.[198] while studying the decomposition of 3,4-substituted pyrazolines observed retention of geometrical configuration and considered this fact as evidence for a concerted mechanism instead of a biradical intermediate. On the other hand, when 3,5-*cis*- or -*trans*-pyrazolines are decomposed, there is an inversion of configuration in the cyclopropanes produced, this fact tending to support somewhat the biradical mechanism.[4]

A related system was studied in the gas phase, the bicyclic 2,3-diazabicyclo[2.2.1]hept-2-ene. It ejected N_2 in a first-order reaction with a rate coefficient of $7.2 \times 10^{14} \exp\{-37\ 300/RT\}$ s^{-1} between 131.5 and 180.8 °C. The partially deuterated analog was studied by Roth and Martin[199,200] who found the reaction to be (139). To explain these results a stepwise mechanism was postulated with a first step in which biradical **56** containing N_2 was produced.



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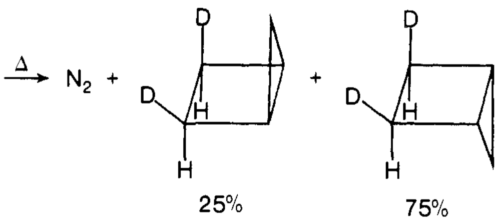
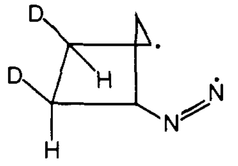


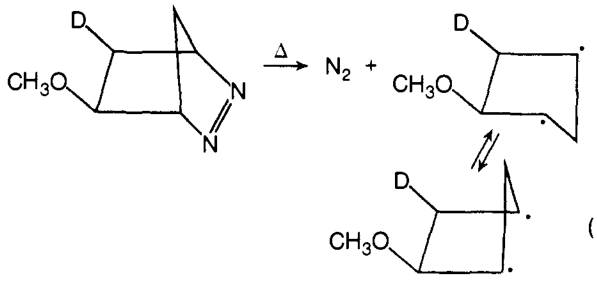
(139)

While the trimethylene biradical postulated by Crawford and Cameron[196] was a planar singlet with both electrons in an antibonding symmetrical orbital in order to explain the results during

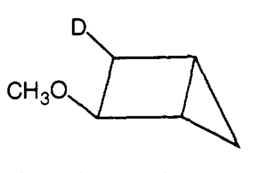


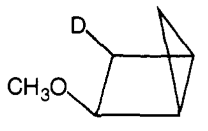
56

the pyrolysis of *exo*- and *endo*-5-methoxy derivatives, Allred and Smith[201] preferred the participation of a pyramidal biradical without N_2 in the first step (reaction 140). This initially formed biradical could then undergo ring closure giving rise to either of the two following products.

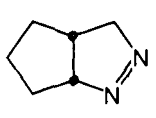


(140)





In order to further elucidate the nature of the structure of the initially formed transition state Schneider and Crawford[202] studied the thermolysis of some 2,3-diazobicyclo[3.3.0]octenes in the gas phase using from 100 to 200 Torr of compound. The compounds studied were **57–59**. The investigators determined the kinetic parameters for the decomposition of these compounds and concluded that the production of the planar biradical would not explain the results obtained, nor would the mechanism of Roth and Martin.[199,200] Therefore the authors put forward two possible mechanisms, Schemes VII and VIII, the latter being analogous to that of Allred and Smith.[201] At the time of the study the evidence was not sufficient to discriminate between the two possible mechanisms. The activation energy for the decomposition of **58** was only 1.3 kcal/mol less than that for the decomposition of **57** in contrast to the 8.8-kcal/mol decrease observed on going from 3-methyl-1-pyrazoline to 3-vinyl-1-pyrazoline (Strausz et al.,[4] Table 7). Schneider and Crawford[202] suggested that considerably more bond breaking has to be achieved to reach the transition state for the bicyclic systems than for the simpler cyclic compounds.



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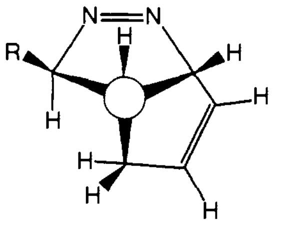


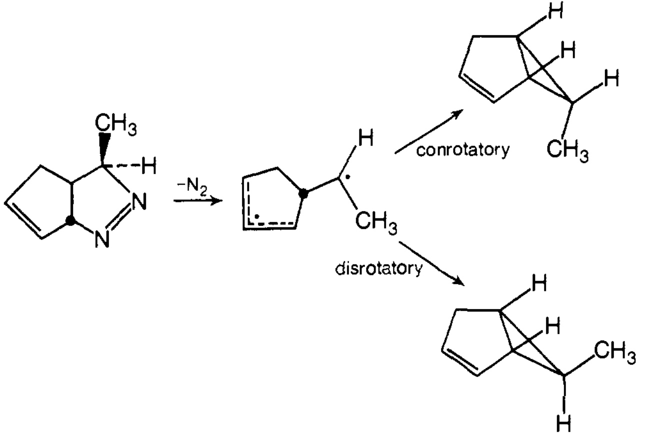
58, R = H
59, R = CH_3

Timberlake and Bandlish[203] studied the thermal decomposition of *trans*-3,5-diphenyl-1-pyrazoline (**57**) and of *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (**58**), and determined the following rate parameters

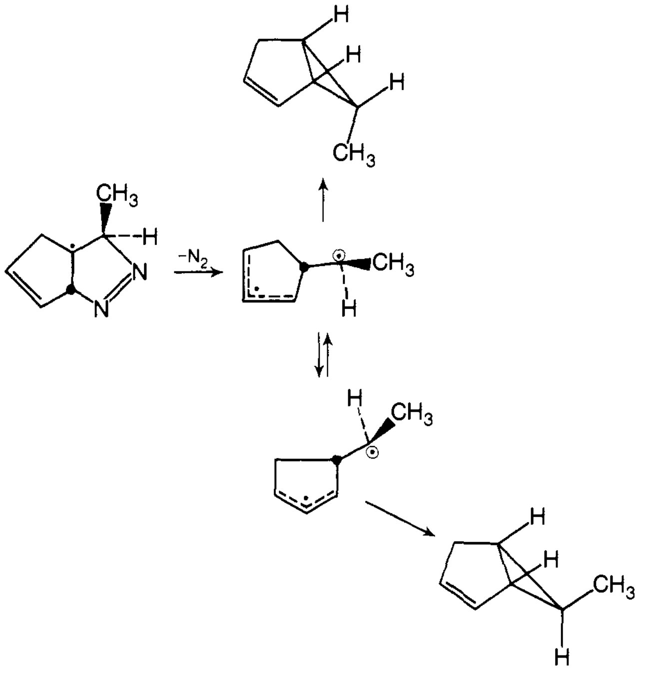
for **57** $\log A\ (s^{-1}) = 14.1$, $E_A = 27.5 \pm 0.5$ kcal/mol
for **58** $\log A\ (s^{-1}) = 14.9$, $E_A = 26.1 \pm 0.6$ kcal/mol

The investigators claimed that since these values agree with those for open azo compounds where the simultaneous fission of the two C–N bonds has been demonstrated, the same mechanism has to be operative in this case. Of course, this is indirect evidence for the one-step N_2 expulsion.

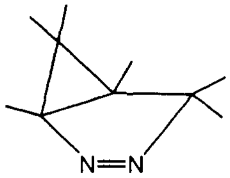
SCHEME VII

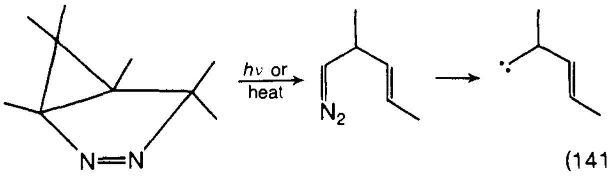


SCHEME VIII



On the other hand, during a study of the gas- and liquid-phase thermal and photochemical decomposition of 2,3-diazabicyclo[3.1.0]hex-2-enes in pentane, Eaton et al.[204] concluded that in these bicyclo azo compounds carbene formation was a major decomposition path (reaction 141) and that this mode of decomposition should be considered competitive with simple N_2 extrusion in strained bicyclic pyrazoline systems. They suggested





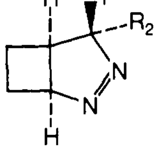
(141)

TABLE X. Activation Parameters for the Decomposition of Three Pyrazolines

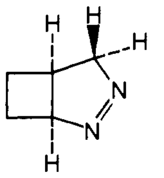
	E_a, kcal/mol	Ref
4-Methylene-1-pyrazoline	32.6 ± 0.3	209
1-Pyrazoline	42.4 ± 0.3	197
3-vinyl-1-pyrazoline	32.2 ± 0.3	196

that this path may also play a role in unstrained monocyclic pyrazoline systems.

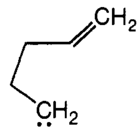
Further evidence against the involvement of the planar trimethylene biradical during pyrolysis of these compounds was claimed by White et al.[205] 4-Methyl-2,3-diazabicyclo[3.2.0]-hept-2-enes **60a** and **60b** were pyrolyzed. Flow pyrolysis in toluene as diluent was used. The system was extremely complex; nine different products were found and no kinetic analysis could be made. Bergman and co-workers had previously pyrolyzed the compound[206]



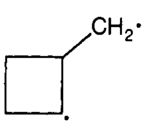
60a, $R_1 = H$, $R_2 = CH_3$
b, $R_1 = CH_3$, $R_2 = H$



and the 6,7-dimethyl analog.[207] In those cases the investigators attributed the different products found to two pathways of decomposition. One pathway was via carbene formation (a) and

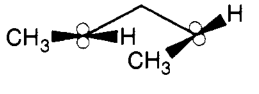


a

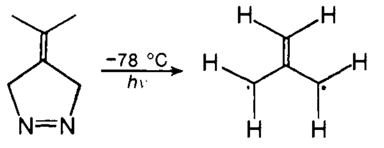


b

the other via diradical formation (b). In the case studied by White et al.,[205] again the two parallel path mechanism was claimed, but for the initial step it was suggested that there is a sequential C–N cleavage and a back-side displacement of N_2 in a nitrogen-containing intermediate. This called into question the postulate of Crawford's group[208] that the following biradical is an intermediate.



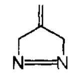
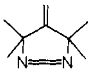
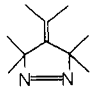
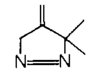
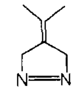
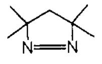
Crawford et al.[209] studied the thermolysis of 4-alkylidene-1-pyrazolines, intending to generate the trimethylenemethane. Taking into account that Dowd[210] detected trimethylenemethane by ESR from the solid-phase photolysis of **61** at −185 °C (eq 142), Crawford et al.[209] said that the triplet could have structure

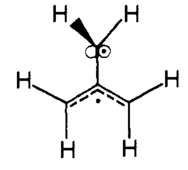


(142)

61 **62**

TABLE XI. Kinetic Parameters for the Gas-Phase Thermolysis of Some Methylenepyrazolines

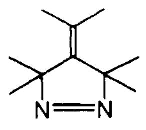
Compound	E_a, kcal/mol	Log (A/s^{-1})	ΔS_{200} (eu)	Rel rate	Ref
	32.6 ± 0.3	13.24	−1.1	62.8	209
	40.7 ± 0.4	15.53	+9.8	1	212
	39.8 ± 0.6	13.6	+0.7	0.031	213
				21	209
				24	209
	37.7 ± 0.4	14.49	4.6	3.0	194



63

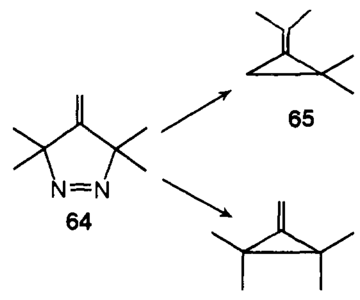
62 or the structure **63**. From analysis of the activation energies for the decomposition of 4-methylene-1-pyrazoline, 1-pyrazoline, and 3-vinylpyrazoline, shown in Table X, it was concluded that the lower activation energy E_a of the 3-vinyl-1-pyrazoline, as compared with that of 1-pyrazoline, reflected the greater stabilization of the radical-like transition state by allylic resonance. In a similar way, the lower value for E_a of methylene-1-pyrazoline compared to 1-pyrazoline reflected a comparable stabilization of the intermediate. As for the detailed mechanism of the thermolysis, the investigators said that more than one mechanism was required to explain all the data. It could also be that the initially produced intermediate had so much excess energy that the observed product distribution was not representative of the mechanism at higher pressures. The investigators favored the possibility that the initially formed intermediate did not include N_2 in it as postulated by Roth and Martin.[200] The same conclusion was drawn from the kinetics of the thermolysis of *cis*- and *trans*-3,5-divinyl-1-pyrazoline in diphenyl ether solution at 35–65 °C.[211] The problem of the excess energy distribution among reaction products will be discussed later, as it is related to the photolysis of these compounds.

The methylene pyrazolines were further studied by Crawford and Tokunaga[212] who studied the 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline and compared the results obtained with those of Engel and Shen[213] for the compound



and with some previous results of their own group. The kinetic parameters for these compounds are shown in Table XI. Specifically for 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline, the second compound listed in Table XI, the Arrhenius parameters were determined between 165 and 200 °C, and the pressure used was 400 Torr of reactant. The reaction scheme was found to be that in eq 143a,b.

Since compound **66** isomerized to compound **65** at least eight times faster than it was produced from **64**, the direct observation of the ratio **66**:**65** was prevented. The investigators intended to



(143a)

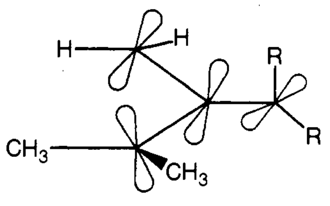
(143b)

64

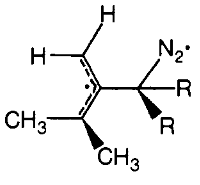
65

66

assess the ratio from kinetic data. From Table XI it can be seen that the replacement of an H by a CH$_3$ reduces the rate of decomposition. The second compound has one-third the rate of the sixth one, thus indicating that the allylic nature of the incipient radical does not accelerate the reaction. This apparently contradicts previous assessments by the same research group when comparing 1-pyrazoline with 3-vinyl-1-pyrazoline,[209] but the investigators found an explanation to this by postulating that neither the second nor the third compound of Table XI can fold to an envelope conformation, due to steric hindrance by the four methyl groups, and thus the intermediate species formed is different in these cases. Still unresolved was the problem of the nature of the biradical formed. It could be **67** (a trimethylene) or **68** (a trimethylene with the N$_2$ attached to it).

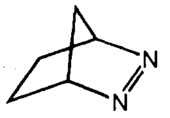


67



68

The mechanism postulated to explain the photochemical behavior of the 1-pyrazoline derivative BDH (2,3-diazabicyclo[2.2.1]hept-2-ene) in the gas phase[214] is shown below. No direct evidence for participation of triplet states was found although triplet states sensitized the decomposition. No phosphorescence was detected. Fluorescence was detected instead. Products of the photochemical decomposition were N$_2$ and the products of ring closure, as in the thermolysis case. The pressure dependence of decomposition and of fluorescence was followed.



$+ h\nu \longrightarrow \mathrm{BDH^*}$ (144)

(BDH)

$\mathrm{BDH^*} \longrightarrow \mathrm{BDH} + h\nu$ (145a)

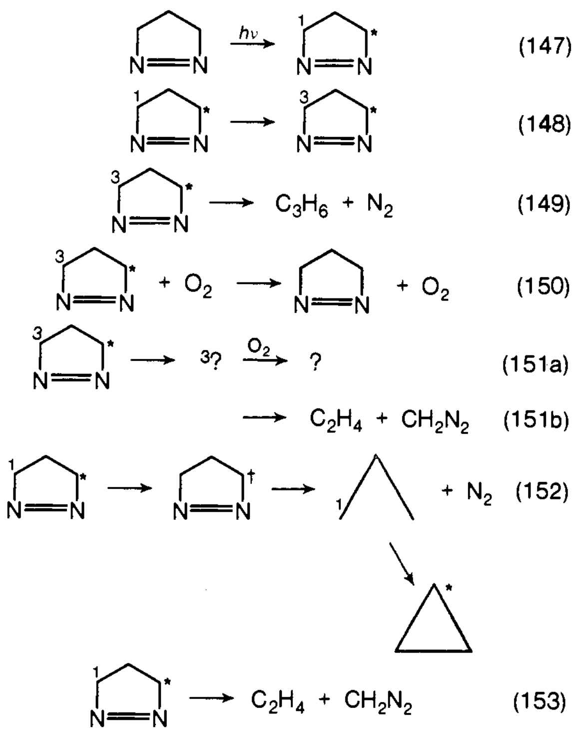
$\longrightarrow$ decomposition (145b)

$\mathrm{BDH^*} + \mathrm{M} \longrightarrow \mathrm{BDH} + \mathrm{M}$ (146a)

$\longrightarrow$ decomposition (146b)

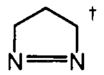
From the analysis of the results obtained as compared with those obtained while studying the photolysis of BDH (2,3-diazabicyclo[2.2.1]hept-2-ene), it was suggested that the dissociative state of BDO (2,3-diazabicyclo[2.2.2]oct-2-ene) lies at higher energy than that of BDH. Moore et al.[215] also have shown that triplet species sensitized the decomposition of 1-pyrazoline, but gave different products from those coming from direct photolysis. It was suggested that direct photolysis gives singlet trimethylene, whereas the benzophenone-photosensitized reaction gives triplet trimethylene as the intermediate. Likewise, it has been shown that triplet quenchers (NO, for instance) do not affect direct photolysis results. Thus direct irradiation gives photodecomposition through singlet states.

SCHEME IX



Cadman et al.[216] studied the photolysis of 1-pyrazoline as a means of producing excited cyclopropane with a definite amount of excess energy in order to study the behavior of the excited cyclopropene. This was done also by Dorer[217] who studied the photolysis of 4-methyl-1-pyrazoline and analyzed the isomeric distribution of the C$_4$ compounds with that predicted by the RRKM theory for unimolecular decomposition of the excited cyclic fragment.

The study performed by Cadman et al.[216] showed that the products were N$_2$, c-C$_3$H$_6$, C$_3$H$_6$, and C$_2$H$_4$. The radiation used was 313 nm. The ratio $[\text{c-C}_3\text{H}_6]/[\text{C}_3\text{H}_6]$ was pressure dependent, while C$_2$H$_4$ yields exhibited only slight pressure dependence. From the analysis of the data it was concluded that C$_3$H$_6$ was formed from at least two sources, only one being pressure dependent. The mechanism is outlined in Scheme IX. The lifetime of the electronic ground state containing about 92 kcal/mol of vibrational energy



was evaluated to be $\tau \simeq 7 \times 10^{-11}$ s. The excited cyclopropane, Δ^*, would contain 75 kcal/mol in excess energy. The products obtained were the same as those obtained upon pyrolysis[194] although in a different distribution. The nature of the product formed in reaction 151a was not clear, nor was its reaction with O$_2$.

In 1971 the 2,3-diazabicyclo[2.2.2]oct-2-ene (BDO) was again photolyzed in the gas phase and in solution at 24 °C.[218] The main conclusions were that the fluorescence occurred from the (n,π^*) singlet state and the decomposition was from the triplet state, in agreement with the mechanism of Cadman et al.[216] The quantum yield for fluorescence was determined to be $\phi_f = 0.56 \pm 0.1$ and the one for decomposition into C$_6$ compounds was $\phi_d\{C_6\} = 0.5 \pm 0.1$ at 0.1 Torr. The emission yield was insensitive to pressure changes, but the decomposition yield varied markedly with pressure. The triplet energy for BDO was determined to be $E_T = 54.5$ kcal/mol by using triplet donors with different triplet energy content.

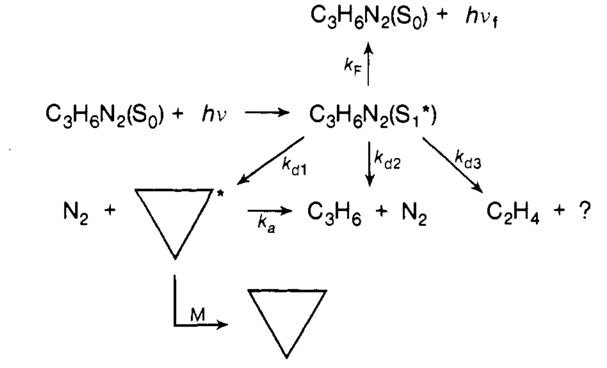
Loper and Dorer[219] again analyzed the photochemistry of 1-pyrazoline. Their main interest was the product energy dis-

TABLE XII. Emission Yields and Lifetimes of 1-Pyrazoline[a]

λ_{inc}, nm	Pressure, Torr	ϕ_I	τ_f, ns
313	0.014	0.004	10
335	0.038	0.150	195

[a] From Loper and Dorer.[219]

SCHEME X



tribution which seemed to be nonrandom and pressure and wavelength dependent. The pressures used were very low to assure that collisional relaxation was negligible. The complete absorption spectrum was determined to consist of two bands, one from 337 to 275 nm assigned to an n → π^* transition and the other extending from 260 to 220 nm assigned to an n → σ^* transition. The onset of emission was located at 312 nm. The 0–0 band was located at 322.9 ± 1.3 nm, and it was claimed that the emission occurs only from the S_1 state. Table XII shows the highest and lowest values obtained for the emission yield of fluorescence (determined using acetone as an actinometer) and for its lifetime for excitation within the first absorption band. During the lifetime measurements a nonexponential decay was observed when $\lambda_{inc} \leqslant 313$ nm. Two possible explanations were put forward for this behavior: (a) different vibronic states were produced on excitation and the emission was from them; (b) intramolecular relaxation was faster than emission and the emission was from different vibronic states produced by intramolecular relaxation. It was very difficult to differentiate between these two possibilities. The quantum yield for decomposition was $\phi_d = 0.7 \pm 0.1$ for 313-nm radiation. The product distribution is shown in Table XIII for 1-pyrazoline and also for 4-methyl-1-pyrazoline.

The mechanism used to explain the results is given in Scheme X. The fluorescence rate coefficient k_f was found to be independent of λ for $\lambda > 315$ nm but $(k_{d1} + k_{d2} + k_{d3})$ increased by increasing vibrational excitation of the produced singlet. Also τ_{nr} (lifetime of the nonradiative processes) begins to fall off at low λ_{inc} and to the investigators this was an indication of intersystem crossing as a route for depletion of the S_1 state. Also, according to the decomposition data, the decrease in τ_{nr} is at least in part due to an increased dissociation rate from the singlet. In any case, it was very difficult to establish how much decomposition occurred from the singlet and how much from the triplet. Vibrational deactivation enhanced fluorescence, thus suggesting that fluorescence occurred from the $S_1{}^0$ level. The mechanism then should be

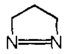
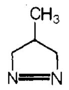
$$C_3H_6N_2(S_0) + h\nu \rightarrow S_1^* \qquad (154)$$

$$S_1^* \xrightarrow{S_0} S_1{}^0 \rightarrow S_0 + h\nu \qquad (155)$$

The lifetime for the singlet state in the high-pressure limit was determined to be 320 ns. Self-quenching of $S_1{}^0$ was found to be unimportant.

The investigators carried out a study of the product composition as a function of pressure at two different wavelengths (313 and 333 nm). The results are shown in Table XIII. The conclusion reached concerning the energy partitioning was that in the long-wavelength range there was statistical intramolecular energy relaxation on fragmentation. However, photolysis in the shorter wavelength region of the first absorption band, where τ_{nr} decreased with increasing excitation energy, resulted in a nonrandom distribution of the available energy.

TABLE XIII. Product Distribution for the Photochemical Decomposition of 1-Pyrazoline and 4-Methyl-1-pyrazoline (from Loper and Dorer[219])

	Excitation wavelength, nm	Total pressure		Δ+ C_3H_6	C_2H_4
	333	$\geqslant 3 + 10$ Torr O_2		98.4	1.6
	333	$\leqslant 10$		97.4	2.6
	333	$\leqslant 0.1$		90	10
	313	$\leqslant 0.3$		82	18
			Δ	Isobutene	Propene
	330	$\geqslant 50$	66	29	5
	313	$\leqslant 0.25$	77	9	14
	Hg (253.7 nm)	320 (N_2)	93	4	3

In a more recent paper[220] the study was extended to 4-methyl-1-pyrazoline (4-MPZ) and *trans*-3,4-dimethyl-1-pyrazoline (TDMPZ) in order to ascertain the effect of added vibrational degrees of freedom remote from the chromophore. For TDMPZ τ_f varies from 380 ns at λ_{inc} 345 nm to 85 ns at λ_{inc} 316 nm. Unfortunately no values for ϕ_f (fluorescence quantum yield) or for ϕ_d (decomposition quantum yield) were reported. Only the relative ratio of the two quantum yields for the two compounds was reported. The investigators postulated that the nonradiative deactivation of the S_1 state of pyrazoline resulted primarily, if not exclusively, in dissociation.

In the low-pressure region the fluorescence lifetime and the nonradiative lifetime were insensitive to the vibrational complexity of the reactant upon excitation by the shorter wavelength within the first singlet band. On the other hand, near the onset of the absorption TDMPZ appeared to show a larger τ_{nr} than PZ. The investigators interpreted these results in terms of a different geometry of the excited state of the two compounds.

Dorer and Pfeiffer,[220] on the basis of their calculations concluded that increasing vibrational complexity did not effectively alter the nonradiative lifetime of the excited state, thus leading them to conclude that intramolecular energy relaxation occurs in the excited state prior to fragmentation or emission.

By analyzing the experimental rate constants for the structural isomerization to the corresponding olefins of the different cyclopropanes produced from the photolyses of the three studied pyrazolines, the investigators concluded that methyl group substitution at a site removed from the reaction center increased the amount of energy in the hydrocarbon fragment by essentially the amount predicted by a statistical model for intramolecular energy relaxation. A statistical model, in which all the available energy is randomly distributed (thermal + light energy + exothermicity at 0 °C), fitted their experimental data, and this was the model used for the long-wavelength region (334 nm). This implied that the electronic excitation energy was converted to vibrational energy of an intermediate that lived long enough to randomly distribute this energy before ejecting the N_2. The lifetime of this intermediate was calculated to be no longer than 10^{-11} s. With 313-nm incident radiation the situation was different, and there seemed to be energy partitioning prior to collisional perturbation of the excited species. There was a nonrandom intramolecular energy relaxation at 313 nm, and methyl substitution did not affect product energy distribution. The change observed suggested to the investigators a change in mechanism at the two wavelengths. Considerations of the geometric changes that must occur when 1-pyrazolines fragment to cyclopropanes and N_2 indicate that simultaneous rupture of the two C–N bonds should result in a large part of the available energy going to the N_2 at higher incident energies, but at lower incident energies, only one C–N bond is ruptured initially. Thus at the lower energy, the reactant molecule can re-form in the ground electronic state, but with retention of all the original energy in vibrational modes. This would be the intermediate postulated in thermolysis and in studies of bicyclic derivatives of pyrazoline.[204,206,221] At shorter wavelengths, on the other hand, less energy appeared in the hydrocarbons, and the internal energy distribution was not affected by substitution. The explanation most plausible to the investigators was that in this case simultaneous rupture of the two C–N bonds occurred prior to intramolecular vibrational relaxation.

It is important to note that the entire edifice of the argument is based on the geometry, the excess energy, and the tightness of binding of the excited state of the different pyrazolines. Crawford et al.[222] studied the direct photolysis, and the mercury-sensitized decomposition of 1-pyrazoline, and also its fluorescence. For the direct photolysis it was found that $\phi = 0.2 \pm 0.08$ with C_3H_6, c-C_3H_6, N_2, and small amounts of C_2H_4 as products. The investigators did not find fundamental differences in calculated geometries for the excited state, thus casting doubts on the deductions of Dorer and Pfeiffer.[220] Crawford et al.[222] were more inclined to see a nonrandom energy distribution of all the excess energy within all the singlet absorption band.

The mechanism postulated in this case was:

$$\mathrm{Py}^{*\dagger} + \mathrm{Py} \rightarrow \mathrm{Py}^{*} + \mathrm{Py}^{\dagger} \qquad (156)$$

$$\mathrm{Py}^{*\dagger} \rightarrow {}^{3}\mathrm{Py} \qquad (157)$$

where † represents vibrational excitation and * represents electronic excitation. One important finding of this study was that increasing the temperature decreased the emission yield. The investigators also studied the $Hg(^3P_1)$ sensitized decomposition. They found that the products were the same as for direct photolysis: c-C_3H_6, C_3H_6, N_2, and small amounts of C_2H_4; ϕ_d (under $Hg(^3P_1)$ sensitization) = 0.5 and

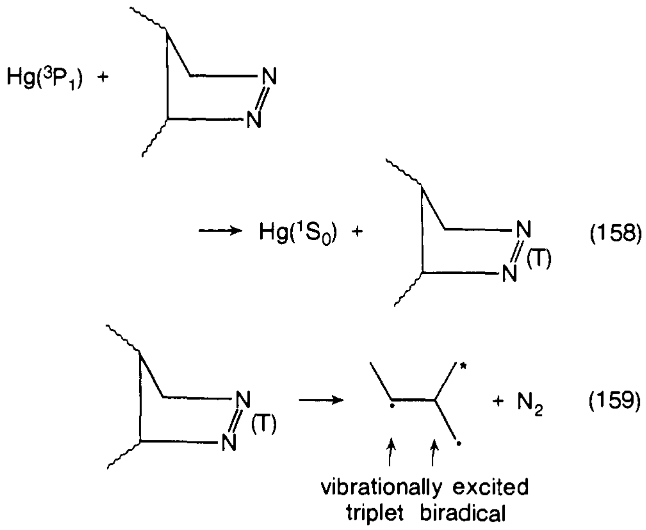
$$(\text{c-}C_3H_6/C_3H_6)_{\text{sensit}} < (\text{c-}C_3H_6/C_3H_6)_{\text{direct photolysis}}$$

The mechanism accounting for this difference was still not clear.

Klunder and Carr[223] thoroughly analyzed the $Hg(^3P_1)$ sensitization of pyrazolines. They studied *cis*- and *trans*-3,4-dimethyl-1-pyrazolines. The major products found for both isomers were N_2, *cis*- and *trans*-dimethylcyclopropane, *cis*- and *trans*-2-pentene, 3-methyl-1-butene, and ethane. No geometrical isomerization of the reactants was detected. Minor products were 2-methyl-1-butene and 2-methyl-2-butene. Some higher molecular weight products (C_8) were also found. The quantum yields were the same for all the products from both isomers. $\Phi\{N_2\} = 0.95 \pm 0.05$ at 5 Torr for the trans and $\Phi\{N_2\} = 0.93 \pm 0.05$ at 4 Torr for the cis isomer. Evidence was given in favor of a triplet biradical intermediate, and the mechanism outlined is shown in Scheme XI. The vibrationally excited biradical could give CH_3 + olefin or be deactivated. The deactivated biradical was thought to give rise only to cyclization. Since the presence of O_2 did not change the cyclic compound yields, the conclusion was that O_2 did not react with deactivated triplet biradicals, and this is a weak point in the argument. Further evidence was given by the investigators to rule out a $T_1^* \rightarrow S$ transition.

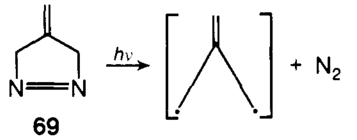
It was also concluded that cyclization of triplet 1,2-dimethylene biradicals occurred at a slower rate than internal rotation, this leading to loss of stereospecificity of the resulting dimethylcyclopropanes, in contrast with the retention or inversion of configuration observed, respectively, upon direct photolysis[216] or on thermolysis.[224] With the postulated mechanism, some of the so far unexplained facts could be understood. Olefins are produced in the direct photolysis of pyrazolines in the gas and liquid phase.[206,216,219] However, in the sensitized decomposition in solution olefin production is greatly reduced as compared with the gas phase. If hot biradicals give olefins, then in the liquid phase they are thermolyzed before decomposition and the olefin production is reduced.

SCHEME XI



The mechanism of olefin production is different in singlet biradicals.[220] For the singlet there is intramolecular rearrangement, which seems to be absent in the triplet biradicals.

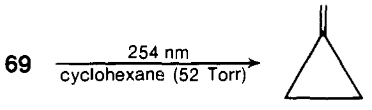
4-Methyl-1-pyrazoline has been the object of photolytic study.[225] Its photodecomposition was studied in the vapor phase by direct irradiation at 327 nm. The only detected product condensable at 78 K was methylenecyclopropane. The mechanism assumed was:



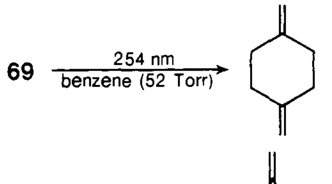
69 (160)

The quantum yield of decomposition was 0.37 ± 0.1 with 1.52 Torr at room temperature, but the quantum yield decreased with higher pressures of added gases. It was assumed that direct photolysis gives a singlet species that closes to methylenecyclopropane.

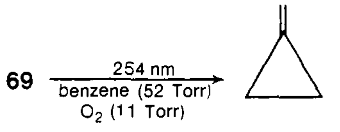
With benzene sensitization (254 nm) a dimer was found together with methylenecyclopropane. The overall reactions for the three conditions used were:



10% reaction (161)

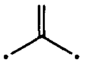


60% reaction (162)



34% reaction (163)

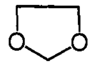
These facts led the authors to conclude that benzene sensitization produced both singlet and triplet species which possibly lead to methylenecyclopropane and the dimer, respectively. It was also said that O_2 quenched the triplet of **69** (which would be in contradiction with the findings of Klunder and Carr[223])



or before the dimer was produced, and that O_2 partially quenched the benzene singlets. The investigators realized that there could be other possibilities to explain their results as well.

2. Dioxolanes

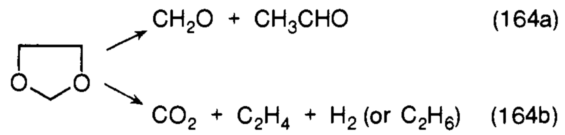
The thermal decomposition of 1,3 dioxolane (**70**) was studied by Guenther and Walters[226] for pressures between 50 and 400



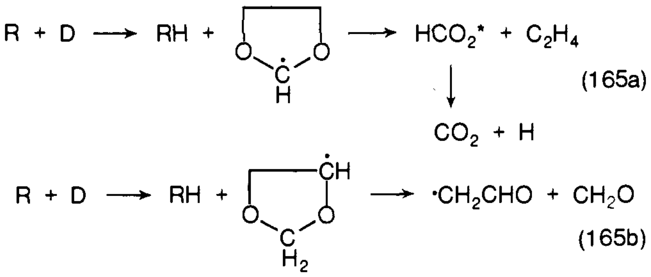
70

Torr and temperatures between 455 and 525 °C. An apparent 1.3 order in reactant was determined, and the final products were found to be CO, H_2, CH_4, CO_2, and C_2H_6.

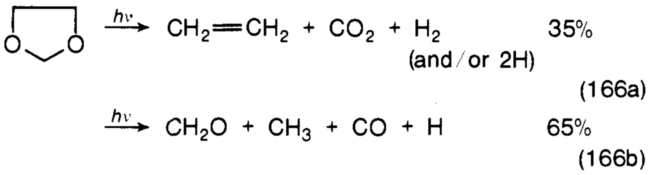
The mechanism outlined consisted of two overall steps: reactions 164a and 164b. CH_2O would afterwards give rise to H_2



and CO and CH_3CHO would convert to CH_4 + CO. Radical participation was also demonstrated since the addition of NO or C_3H_6 quenched 80% of the reaction. Somehow H atoms or $\cdot CH_2CHO$ radicals would be produced and abstract from the dioxolane (D) according to reactions 165a and 165b, where R could be either H or $\cdot CH_2CHO$. These two steps (165a and 165b) would give rise to a chain mechanism.



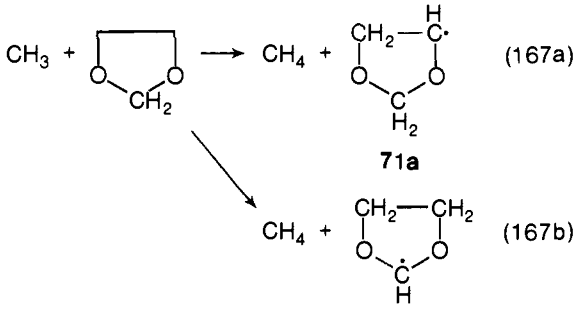
Roquitte[227] studied the gas-phase photolysis of dioxolane. The temperatures used ranged from 27 to 110 °C. The effective wavelengths used were those below 200 nm coming from an unfiltered medium-pressure mercury arc. The principal products found were H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, $n\text{-}C_4H_{10}$, and CH_2O. The yield of all the products except CO increased with temperature. Since C_2H_4 had a pronounced scavenging effect on H_2 production, H atoms were postulated as being produced in a primary act, this being in agreement with previous postulates for the thermal study. At least two primary processes were thought to occur: reactions 166a and 166b. The possible for-



mation of $\cdot CH_2CH_2O$ and its further decomposition into either CH_3 + CO + H or C_2H_4 + O was postulated, in order to correlate with the investigator's findings in the ethylene oxide system.[17] The very initial act was thought to be either the formation of the $\cdot OCH_2OCH_2CH_2\cdot$ biradical or of the $\cdot OCH_2CH_2OCH_2\cdot$ biradical.

Since the energy absorbed by the dioxolane molecule was about 144 kcal/mol or greater, and the C–O bond dissociation energy is only 75–80 kcal/mol the initially formed biradicals would be highly energetic and would break down immediately, and thus the molecular products were not eliminated in the presence of O_2.

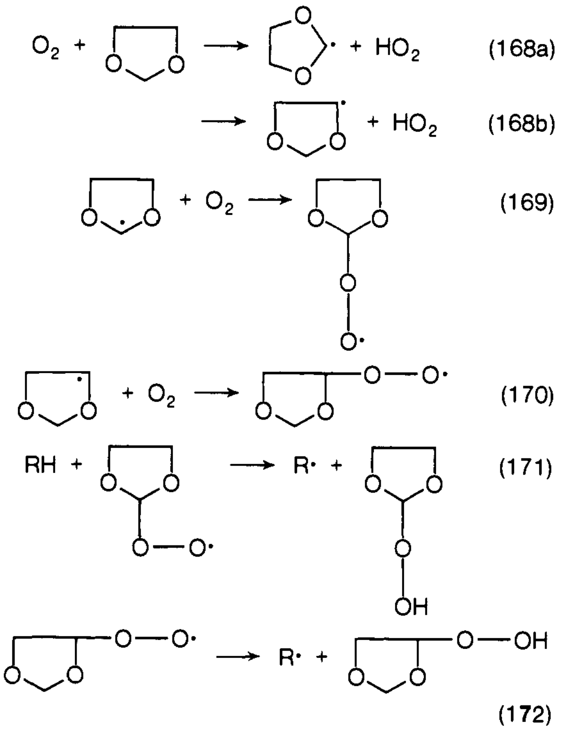
Methyl radicals from azomethane photolysis were added to the system in order to analyze the fate of the biradicals **71a** and **71b** formed by H-atom abstraction from a CH_2 group by the CH_3 radicals formed in the dioxolane system itself (eq 167a,b). It was found that **71b** was produced in larger amounts than **71a**.

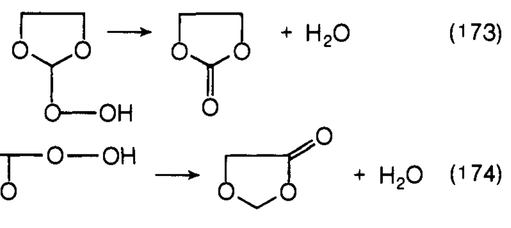


71b

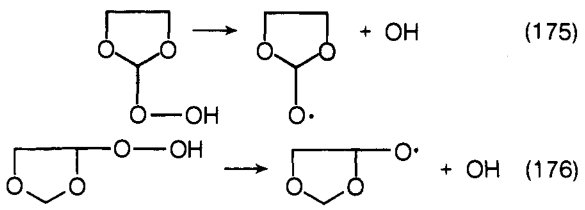
In 1971 the gas-phase oxidation of 1,3-dioxolane was studied.[228] The pressures used were always below 1 atm and the temperature was between 240 and 340 °C. Explosions were found to occur and the explosion limits were determined. The mechanism proposed is given in Scheme XII. Finally the hydroperoxides would decompose giving rise to the two keto compounds found in the system (eq 173 and 174).

SCHEME XII





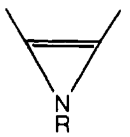
On the basis of kinetic arguments it was concluded that the hydroperoxides formed in reactions 171 and 172 were the main chain branching agents for low-temperature oxidations. The branching steps would be (175) and (176). At higher temperatures the importance of the hydroperoxides would be smaller. Of course heterogeneous reactions were found to be important. More evidence was found from ^{14}C labeling experiments,[229] but the system is not completely resolved yet.



C. Three Heteroatoms

1. Triazoles

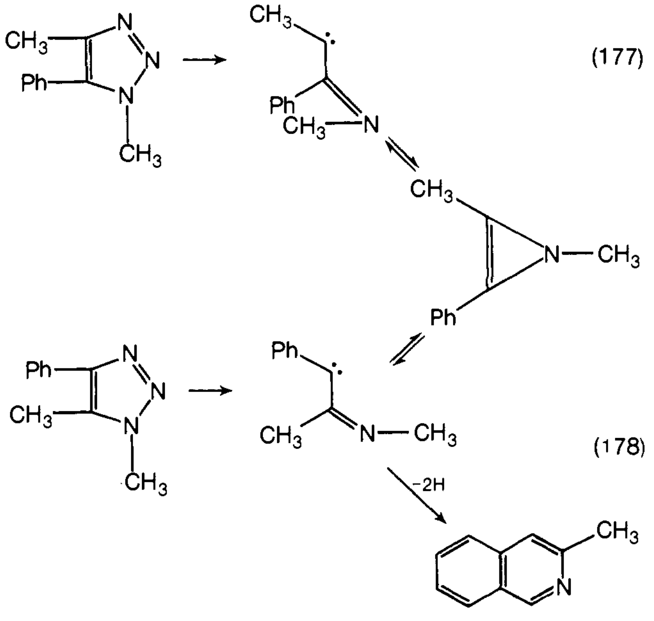
The vacuum pyrolysis of a series of 1-R-1,2,3,-triazoles was studied by Gilchrist et al.[230] In each case the products were N_2 and a series of different compounds (depending on the original triazole used). After a detailed analysis of the products, the investigators ruled out a concerted mechanism and in each case found a mechanism involving 1-R azirines to explain the results.



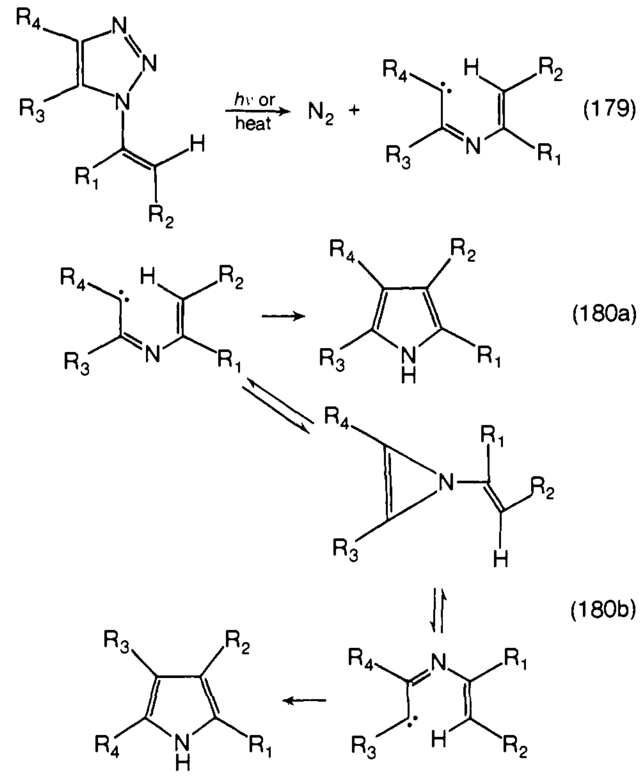
In fact they claimed that the first intermediate formed was an iminocarbene formed both by the action of light or heat. The iminocarbene would then give the 1-H azirine by rearrangement and afterwards it would give the final products. For 1-methyl-1,2,3-triazoles the mechanism proposed is shown in Scheme XIII. A slightly more complex mechanism was needed for 1-vinyl-1,2,3-triazoles (Scheme XIV).

In a further paper of the series the same research group[231] studied the pyrolysis of phenyl-substituted 1,2,3-triazoles in the 1, 4, and 5 positions using ^{13}C-labeled compounds. Several products were found which included scrambling of the labeled carbon atoms. Thus further confirmation was obtained for the intermediacy of the iminocarbenes and 1-R azirines.

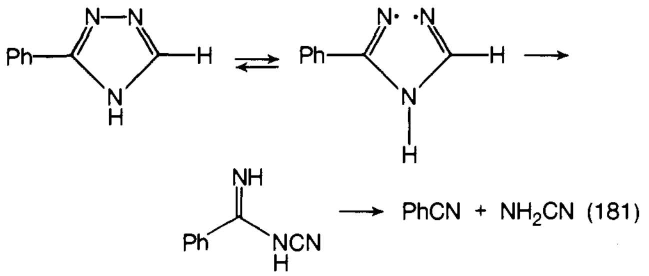
SCHEME XIII



SCHEME XIV

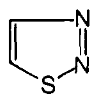


The 1,2,4-triazoles were pyrolyzed at 600–800 °C by Gilchrist et al.[232] in a third study. The conclusion reached was that phenyl-substituted 1,2,4-triazoles have two routes for thermal fragmentation. One involves rearrangement followed by N_2 extrusion as with the 1,2,3-triazoles. The other route involves N–N bond cleavage followed by extrusion of a nitrile fragment which might proceed as shown (eq 181). Increased phenyl substitution would favor this route. The two routes, the one involving arizine formation and the one involving nitrile extrusion, would be energetically similar.



2. Thiadiazoles

Strausz and co-workers[49] photolyzed 1,2,3-thiadiazole (**72**) and 5-methyl-1,2,3 thiadiazole (**73**) in the presence of perfluorobutyne-2 and found good yields of 2,3-bis(trifluoromethyl)thiophenes. This was taken as evidence for the ejection of N_2 and the involvement of a thiirene intermediate during the photolysis of the thiadiazolic compounds. Zeller and co-workers,[233-235] on the other hand, postulated the production of a biradical during their study of the gas-phase and solution photolysis of the same compounds. The initial step would then be (182), and then this might be followed by ring closure to give the thiirene. In fact, Krantz and Laureni[236] recently photolyzed the



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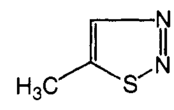
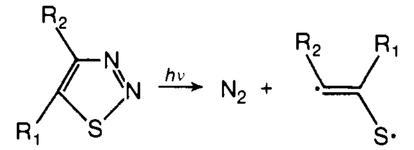
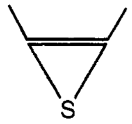


73



(182)

1,2,3-thiadiazole in a matrix and gave evidence for the involvement of thiirene



as a precursor of the observed photoproduct HC≡CSH. Torres et al.[237] also recently have found preliminary evidence for the thiirene intermediate in the photolysis of *tert*-butyl-monosubstituted thiadiazoles. Thus the decomposition of 1,2,3-thiadiazoles seems to be analogous to that for 1,2,3-triazoles. However, Krantz and Laureni[236] also presented evidence for the formation of thioketene (H_2CS) in the 1,2,3-thiadiazole system, thus indicating a second route for the photodecomposition or that the thioketone is produced via the unstable thiirene.

Seybold and Heibl[238] studied the gas-phase flash thermolysis of several substituted thiadiazoles at 580 °C and 10^{-4} Torr pressure and found thioketones in 60–75% yield. The different thioketones were identified by several methods: ultraviolet, infrared, nuclear magnetic resonance, and mass spectroscopy, as well as by chemical behavior.

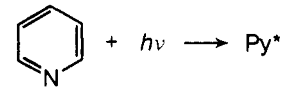
V. Six-Atom Rings

A. One Heteroatom

1. Nitrogen Compounds

Noyes and Al-Ani[239] have recently reviewed the photochemistry of pyridine, picolines, and diazoles as part of the photochemistry of simple aromatic molecules in the gas phase. We will mention, however, the main features of the gas-phase reactions of these compounds.

Pyridines. The gas-phase photolysis of pyridine was thoroughly studied by Mathias and Heicklen[240] between 25 and 260 °C with direct radiation of 213.9 and 228.8 nm. Hg($^3P_1$) photosensitization at 250 °C also was used. The effects of added O_2 and NO and of pyridine pressure changes were investigated. Acetylene and acrylonitrile (C_3H_3N) were determined as coming molecularly from the primary decomposition of the excited pyridine, while the other products [H_2, CH_4, C_2H_4, C_3H_6, allene, methylacetylene, isobutylene, an unknown compound, polymer, and HCN (and/or C_2N_2)] were produced through secondary reactions. The mechanism outlined for direct irradiation was:



(Py)

(183)

$$Py^* \rightarrow C_2H_2 + C_3H_3N \tag{184}$$

$$Py^* + Py \rightarrow 2Py \tag{185}$$

$$Py^* + M \rightarrow Py + M \tag{186}$$

$$C_3H_3N \rightarrow \text{polymer} \tag{187}$$

$$C_3H_3N + h\nu \rightarrow C_2H_2 + HCN \tag{188}$$

$$2C_3H_3N + h\nu \rightarrow 2C_2H_2 + C_2N_2 + H_2 \tag{189}$$

where Py* simply represents the excited pyridine, and reaction 189 is composed of several elementary steps. It was found that reaction 187 dominated at room temperature, while reactions 188 and 189 were more important at higher temperatures. The ratio k_{185}/k_{184} was found to vary with temperature and wavelength. Table XIV summarizes the results.

TABLE XIV. Photolysis of Pyridine[a]

λ, nm	Temp, °C	k_{185}/k_{184}, Torr^{-1}	k_{186}/k_{184} NO	k_{186}/k_{184} O$_2$
253.7	25	2.60×10^3		
228.8	25	3.22×10^4	5.06×10^3	2.67×10^3
228.8	~262	51	5.73	4.69
213.9	25	25.0	2.02	1.38
213.9	~262	3.23	0.170	0.095

[a] From Mathias and Heicklen.[240]

From an analysis of the temperature and wavelength dependence of the rate constants ratios it was concluded that the rate of excited pyridine unimolecular decomposition depended on the excess energy it had, be it thermal or photochemical. That is, k_{184} increased with total energy content of pyridine, similar to the thiophene case.[172]

It was claimed that an isomer of pyridine was produced, but no reaction for its production was postulated. It might be a unimolecular rearrangement of Py*. The nature of Py* was not fully analyzed.

The processes taking place during the Hg sensitization were different from those occurring during direct irradiation, and this is an indication of small participation of the triplet in the direct irradiation case. This is in agreement with the quantum yield for intersystem crossing into the triplet state determined by Lemaire.[241] He, as well as Cundall et al.,[242] determined the yield of triplet production by intersystem crossing using the olefin isomerization technique. Cundall et al.[242] found a triplet yield of 0.36 ± 0.03 under a variety of conditions at 22 °C, but Lemaire[241] found that yields of triplet production in the (n,π*) and in the (π,π*) bands were very low, being higher in the (n,π*) than in the (π,π*) band. The triplet yields for various incident wavelengths were: 240.0–253.7 nm, 0.010 ± 0.001; 265.0 nm, 0.030 ± 0.003; and 275.0–278.0 nm, 0.14 ± 0.01. As Noyes and Al-Ani[239] stated, some ill-defined path must be responsible for the return of the triplet and excited singlet states to the ground state. This path cannot be the decomposition or the isomerization since their quantum yields are extremely low. It cannot be emission either, since no emission has been found for pyridine in spite of many efforts to see it.

The nature of the triplet state produced in Hg sensitization[240] or intersystem crossing[241,242] is not clear either. Evans[243] observed a triplet state on absorption and assigned a (π,π*) nature to it on the basis of very small solvent shifts.

According to Hoover and Kasha,[244] it is still possible that the lowest triplet be (n,π*) and not (π,π*), since the lowest singlet is (n,π*). These last investigators measured luminescence of substituted pyridines, especially with CN and CH_3 groups, in glassy matrices. Strong (π,π*) emissions of long lifetime and strong (n,π*) emissions of short lifetime were observed. Since pyridine itself does not emit, this was taken as an indication of an (n,π*) nature of the triplet state, with a high rate of radiationless transition to the ground state.

More recently, Hotchandani and Testa[245] have measured the phosphorescence and its polarization of aminopyridines, in glassy matrices of four different solvents, irradiating them with 285- and 254-nm radiation. Evidence was presented in favor of a (π,π*) nature for the triplet state, and it was observed that the intersystem crossing was strongly dependent on the nature of the solvent, which raises doubts about the conclusions reached when comparing these solid-state studies with those in the gas phase. It was also said that the solvent could even cause an inversion in the order of the (n,π*) and (π,π*) triplet levels. Hotchandani and Testa[245] said that for other N-containing heterocycles like pyrazine or pyridine, the lowest triplet is an (n,π*) one.

TABLE XV. 2-Picoline Sensitized Emission of Biacetyl[a]

λ, nm	2-Picoline pressure, Torr	ϕ\{triplet\}
248	1	0.031
266	1	0.080
275	6	0.120
280	6	0.210

[a] From Roebke.[247]

Al-Ani and Phillips[246] briefly reported some results on biacetyl emission sensitized by perfluoropyridine using 248-, 254-, and 265-nm radiation. The first two wavelengths did not produce any emission from biacetyl; the third one produced a very weak phosphorescence. No direct emission from the substituted pyridine was found so ϕ_f was claimed to be $\ll 10^{-3}$. Since the ratio of fluorescence to phosphorescence of biacetyl was not measured, it was not possible to determine whether the emission came from intersystem crossing from singlet biacetyl or from a triplet–triplet energy transfer from the heterocycle to biacetyl.

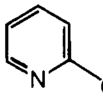
The gas-phase photolysis of 2-picoline (2-methylpyridine) was studied by Roebke.[247] No emission could be detected for excitation between 240 and 300 nm either in the gas phase or in solid matrices. Absorption into the (π,π^*) or (n,π^*) states in the liquid phase or into the (n,π^*) state in the gas phase did not produce products, but absorption into the (π,π^*) state in the gas phase did. The products found were the isomers 3-picoline and 4-picoline in a ratio of about 12:1. The quantum yields of both isomers depended on the wavelength and on the light intensity used.

Triplet state participation was inferred because of the high quenching efficiency of both O_2 and *cis*-butene-2 on the product yields. The triplet yields were determined by adding biacetyl and monitoring its sensitized phosphorescence.

Biacetyl-sensitized phosphorescence was used, and Table XV shows the yields of triplet formation using this method.

The triplet lifetime of picoline was estimated to be $\tau_T \sim 10^{-7}$–10^{-8} s because of the high biacetyl pressures required to observe sensitized biacetyl emission.

The following mechanism was postulated to account for the results:



(Pic)

$$+\ h\nu \longrightarrow {}^1\mathrm{Pic_v} \qquad (190)$$

$$ {}^1\mathrm{Pic_v} \rightarrow \mathrm{I} \qquad (191a)$$

$$ {}^1\mathrm{Pic_v} \rightarrow {}^1\mathrm{Pic_e} \qquad (191b)$$

$$ {}^1\mathrm{Pic_v} + \mathrm{X} \rightarrow {}^1\mathrm{Pic_e} + \mathrm{X} \qquad (192)$$

$$ {}^1\mathrm{Pic} \rightarrow {}^3\mathrm{Pic} \qquad (193)$$

$$ \mathrm{I} + \mathrm{wall} \rightarrow \mathrm{Pic} \qquad (194)$$

$$ \mathrm{I} + {}^3\mathrm{Pic} \rightarrow \mathrm{isomers} \qquad (195)$$

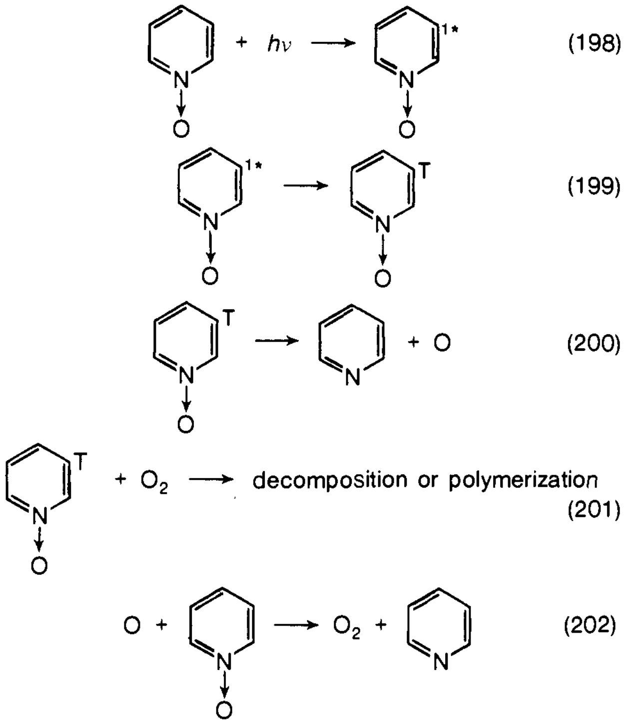
$$ \mathrm{I} + h\nu \rightarrow \mathrm{isomers} \qquad (196)$$

$$ {}^3\mathrm{Pic} + \mathrm{X} \rightarrow \mathrm{Pic} + {}^3\mathrm{X} \qquad (197)$$

where $^1\mathrm{Pic_v}$ is the first excited singlet state also containing vibrational excitation, $^1\mathrm{Pic_e}$ is the same electronic state but thermally equilibrated, $^3\mathrm{Pic}$ is the triplet state, and X is a quenching gas. Reaction 191b was written as first order and means merely that intramolecular energy has been redistributed in such a way that the reverse reaction is unlikely. Reaction 194 was included to account for the wall and surface effects observed. I was an intermediate whose nature was not clear, but a prismane structure was assigned to it. The mechanism is still not clear; not too clear either is its relationship with the pyridine case.

N-Oxides. The picoline and pyridine *N*-oxide photolyses were studied by Hata[248,249] and Hata and Tanaka.[250] For the pyridine *N*-oxide[250] case, the wavelengths used were 326.1 nm, producing a (n,π^*) transition and 253.7 producing a (π,π^*) transition, according to the investigators. The nature of the transitions has been questioned in more recent years.[251] We will discuss this point below.

With both wavelengths the principal product was pyridine. With 326.1-nm incident radiation its quantum yield increased with temperature, but it did not change between 60 and 140 °C with 253.7-nm radiation. The mechanism proposed was the following, involving as the first step the cleavage of the N–O bond.



(198)

(199)

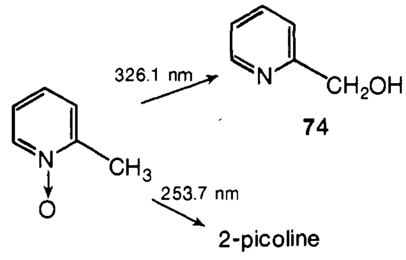
(200)

(201)

(202)

The explanation given for the difference in behavior with temperature of Φ\{Pyr\} at the two wavelengths was that since the dissociation energy for the N–O bond was estimated as about 110 kcal/mol, with 253.7 nm the energy is more than enough, but with 326.1 nm (equivalent to 87.3 kcal/mol) an activation energy is required to cross over to the dissociative triplet state. However, the temperature dependence at 326.1 nm indicated an activation energy of 11.9 kcal/mol, which would be insufficient to reach the estimated bond energy of 110 kcal/mol. An alternative possibility for pyridine production is that an excited pyridine *N*-oxide molecule collides with a ground-state molecule to produce O_2 and two pyridine molecules. This would require only about 102 kcal/mol of energy.

In the 2-picoline *N*-oxide case, instead, two different products were formed when different wavelengths were used:[248,250] 2-pyridinemethanol (**74**) and 2-picoline. The temperature range



74

(203a)

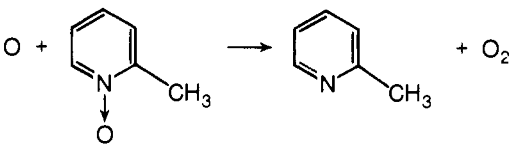
(203b)

used in this case was 50–160 °C, and it was observed that the quantum yield of 2-picoline increased with temperature ranging from 0.4–0.5 at 50 °C to 0.9–1.0 at temperatures >100 °C with

TABLE XVI. Kinetic Parameters for Thermal Decomposition of 3,4-Dihydro-4*H*-pyrans (DHP)

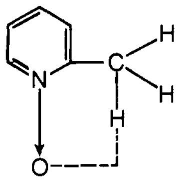
Compound	Temp range, °C	Log (A/s^{-1})	E_a, kcal/mol	Product	Ref
DHP	316–389	14.63	52.43	C_2H_4 + CH_2=CHCHO	254
DHP	450–508	12.81	46.97	C_2H_4 + CH_2=CHCHO	255
6-Me-DHP	330–370	14.45	51.20	C_2H_4 + methyl vinyl ketone	256
2-MeO-DHP	296–353	14.42	48.54	methyl vinyl ether + acetaldehyde	252
trans-2-Me-DHP	287–345	14.25	48.15	methyl vinyl ether + crotonaldehyde	257
cis-2-Me-DHP	287–345	13.96	46.85	methyl vinyl ether + crotonaldehyde	257

253.7-nm radiation.[248] The mechanism postulated in this case was similar to the pyridine *N*-oxide case but an energy of activation for 2-picoline production at 253.7 nm of 1.1 kcal/mol was determined. This was attributed to reaction 204. This would be



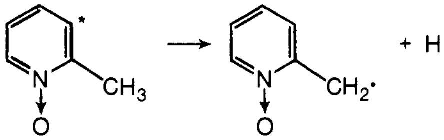
(204)

similar to reaction 202 for the pyridine *N*-oxide case. The explanation for the activation energy in the picoline *N*-oxide case was the formation of a hydrogen bond between the CH_3 and the O, which has to be broken in order to abstract the O atom. The



same explanation could be advanced for the reaction of the excited-state molecule with the ground-state molecule to produce O_2.

At 253.7 nm, H_2 was also found and was explained through reactions 205 and 206. With 326.1-nm radiation, isomerization



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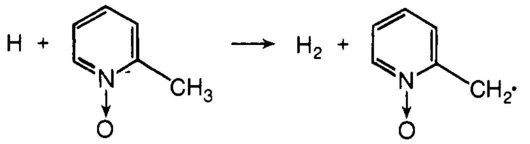


(206)

to **74** was thought to occur from the triplet state with an activation energy of about 3.4 kcal/mol. Hata[248] said that the other processes also occurred at this wavelength but to a lesser extent than the isomerization.

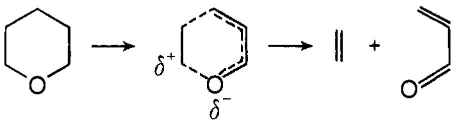
In order to further substantiate the postulate of the bridged form, the photolysis of 3-picoline *N*-oxide was performed in the gas phase.[249] In this case, the interactions of the CH_3 with the O could be neglected. In fact, the main product found was 3-picoline at the two wavelengths employed, 326.1 and 253.7 nm. Here again, as in the pyridine *N*-oxide case, the quantum yield varied with temperature at 326.1 nm, but did not vary at 253.7 nm. Thus 3-picoline *N*-oxide photodecomposes analogously to pyridine *N*-oxide, and similar mechanisms were envisioned. Apparently 2-picoline *N*-oxide is a special case, and the postulate of internal bonding between the methyl group and the oxygen atom in this molecule is supported.

The problems of the nature of the excited states produced have been analyzed more recently by Seibold et al.[251] It was concluded that in the 330-nm band the transition was of a (π,π^*) nature ($A_1 \rightarrow B_1$ transition), with the possibility of some contribution of the (n,π^*) transition. In the 280-nm band the assignment was of a (π,π^*) nature ($A_1 \rightarrow A_1$ transition) as was proposed by Hata[248,249] and Hata and Tanaka.[250]

2. Oxygen Compounds

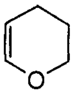
Pyrans. The thermal decomposition of 3,4-dihydro-2*H*-pyrans (DHP) with different substituents has been the object of several studies. All the thermal decompositions are homogeneous first-order processes. In every case the products were almost exclusively an olefin and a carbonyl compound. The results of the several studies are listed in Table XVI. Frey et al.[252] concluded that the mechanism for the decomposition should be a concerted one, involving a slightly polar transition state in which the C–O bond is more cleaved than the C–C bond.

The general scheme would be the following:



(207)

Srinivasan[253] studied the Hg($^3P_1$) sensitization of the decomposition of the 3,4-dihydro-2*H*-pyran (**75**) and of the 2,5-dimethyl-3,4-dihydro-2*H*-pyran-2-carboxaldehyde (**76**). This work



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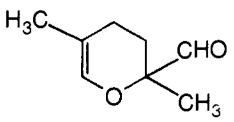

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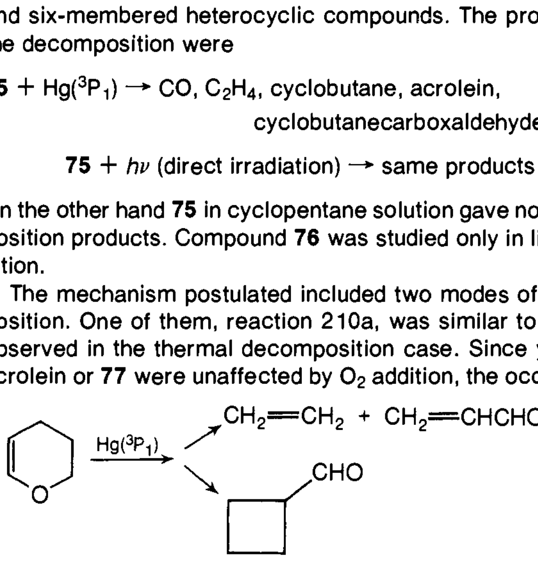
extended the previous studies on photolysis of five-membered and six-membered heterocyclic compounds. The products of the decomposition were

75 + Hg($^3P_1$) → CO, C_2H_4, cyclobutane, acrolein, cyclobutanecarboxaldehyde (208)

75 + $h\nu$ (direct irradiation) → same products (209)

On the other hand **75** in cyclopentane solution gave no decomposition products. Compound **76** was studied only in liquid solution.

The mechanism postulated included two modes of decomposition. One of them, reaction 210a, was similar to the one observed in the thermal decomposition case. Since yields of acrolein or **77** were unaffected by O_2 addition, the occurrence

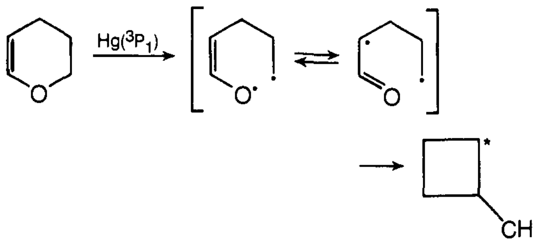


(210a)

(210b)

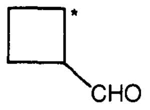
77

of a concerted intramolecular contraction was postulated, or the alternative biradical formation to produce a biradical intermediate not quenched by O_2 (eq 211). The nature of the excited states

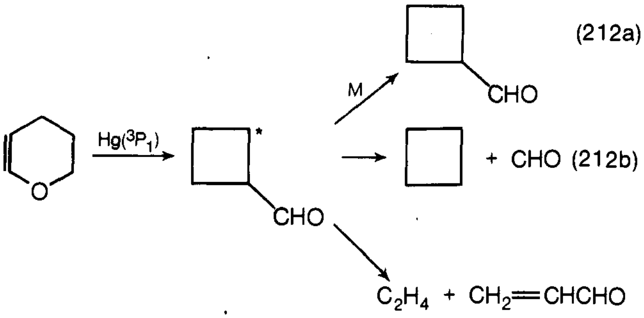


(211)

produced was the object of some speculation by Srinivasan.[253] He thought that an excited



would be produced, analogous to the three-membered ring intermediate formed in the photolysis of five-membered heterocyclic compounds, and it could afterwards undergo three different processes, eq 212a–c. If the initially formed excited state

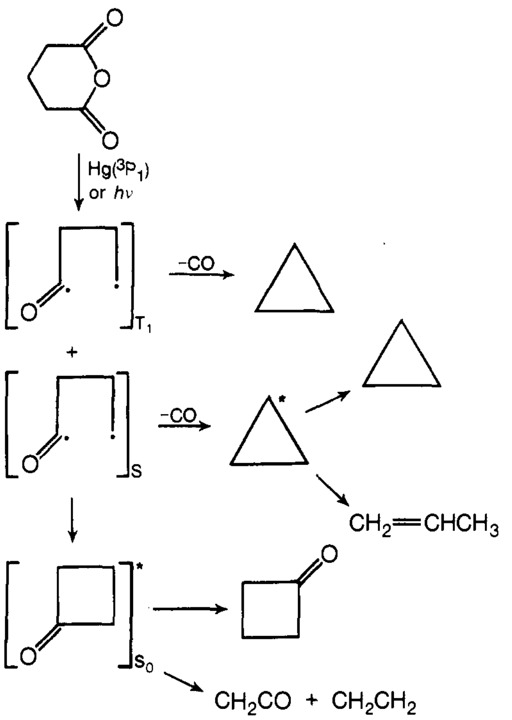


(212a) (212b) (212c)

produced from Hg(6^3P) sensitization is a triplet, it is not clear why the product yields are not quenched by the addition of O_2. Srinivasan[253] pointed out that there was no evidence for an electronically excited state of the dihydropyran, perhaps only highly vibrationally excited ground-state molecules are produced. Such a mechanism is consistent with the pyrolysis of both dihydropyran and cyclobutanecarboxaldehyde whch give ethylene and acrolein as products. This hypothesis needs to be tested experimentally.

Anhydrides. The photodecarboxylation of glutaric anhydride can be formally treated as an heterocyclic compound decomposition. It was studied by Hiraoka[258] who found that Hg($^3P_1$) sensitization and direct irradiation with either a medium-pressure mercury arc or a Zn lamp yielded the same results, thus implying the same intermediate species in the three cases. The mechanism proposed is shown in eq 213a–c. The photolyses of substituted glutaric aldehydes gave analogous results.

The nature of the excited states produced with the anhydrides might be different, however, from those produced in the pyran case, since the presence of the C=O groups in the ring must produce gross perturbations in the energy levels of the excited states. It is worth noting that in the Hg($^3P_1$) sensitization case the excited singlet state was implied.[258] However, it seems more likely that decomposition is occurring from excited vibrational levels of the ground electronic state in both the pyran and anhydride photolyses.

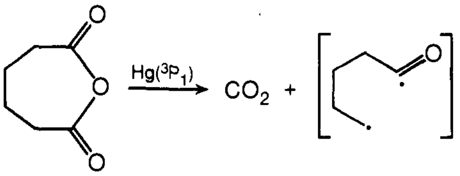


(213a)

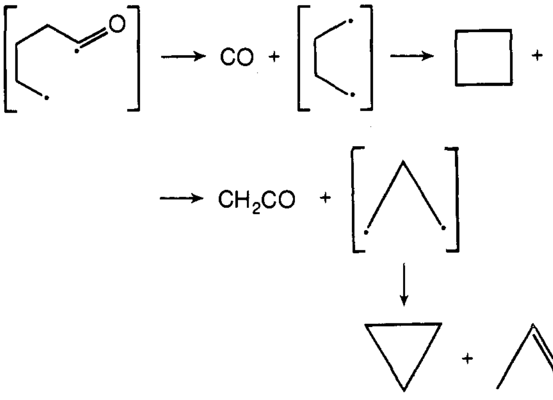
(213b)

(213c)

The fact that the photolyses of cyclic anhydrides give rise to both decarbonylation and decarboxylation of the compounds was already pointed out by Krull and Arnold,[191] who proposed the formation of a biradical as a general intermediate for the Hg($^3P_1$) sensitized decomposition of these compounds (see eq 131). They proposed, however, for glutaric and adipic anhydrides the initial step (illustrated for adipic anhydride, eq 214), giving the biradical which then would lose CO to give the nonoxygenated intermediate and cyclobutane or H_2C=CH_2 (reaction 215a) or would fragment according to reaction 215b. These are similar reactions to those proposed by Hiraoka.[258] These mechanisms need further experimental verification.



(214)



(215a)

(215b)

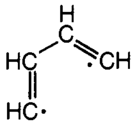
B. Two Heteroatoms

1. *Diazines*

The 1,2-diazine (pyridazine) was photolyzed by Fraser et al.[259] over the temperature range 100 to 160 °C with wavelengths of 365.0 to 366.3 nm. The products found were N_2 and vinylacetylene, their quantum yields at 110 °C being 0.12 ± 0.05 and 0.09 ± 0.04, respectively. Added gases inhibited the decomposition, but O_2 was no more efficient than other gases. Furthermore *cis*-2-butene was not isomerized. Consequently there was no evidence for the participation of a triplet state. Thus it appears that decomposition occurs directly from the excited singlet state which was considered to result from an ($n \rightarrow \pi^*$) transition.[260,261] This state could also be quenched by added gases. The photodecomposition was thought to give rise to a vibrationally excited biradical which could rearrange to vinylacetylene

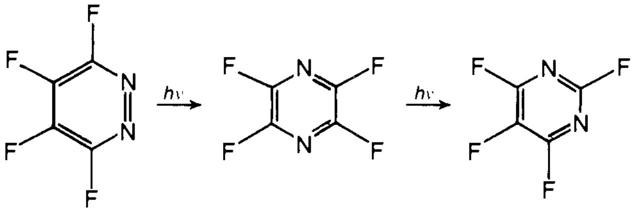
$$[C_4H_4N_2]^* \rightarrow N_2 + [\cdot C_4H_4\cdot]^* \rightarrow CH{\equiv}C{-}CH{=}CH_2 \quad (216)$$

where $[\cdot C_4H_4\cdot]^*$ would be a vibrationally excited species.



The pyridazine can undergo two (n,π*) transitions, though one of them is symmetry forbidden. Therefore absorption leads to the allowed (n,π*) state.[260] Vibrational deactivation of this state is rapid and so is the photophysical electronic relaxation of this state, which accounts for the low fluorescence and photodecomposition yields.

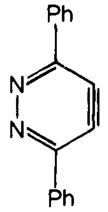
Johnson et al.[262] found that the ultraviolet irradiation of tetrafluoropyradizine in either the vapor phase or solution yields tetrafluoropyrazine which in turn photoisomerizes more slowly to the tetrafluoropyramidine (eq 217). These results agree with



(217)

those of Lahmani and Ivanoff[263] with the nonfluorinated pyrazine and its methyl derivatives. They irradiated the vapors of these compounds at 253.7 nm (π → π*) and 313.0 nm (n → π*). Only in the former case was photoisomerization observed, and the sole product was the corresponding pyramidine.

The fragmentation of 3,6-diphenyl-4,5-dehydropyridazine, when generated in the vapor phase, was observed by Gilchrist et al.[264] It was found that it was a very unstable compound giving rise to N_2 and an acetylene derivative according to reaction 218.



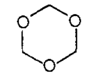
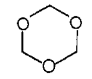
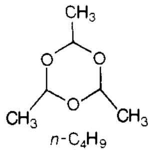
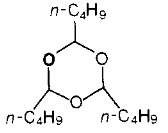
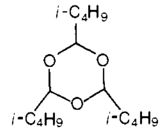
$$\rightarrow N_2 + PhC{\equiv}C{-}C{\equiv}CPh \quad (218)$$

Since Noyes and Al-Ani[239] published their review where the 1,4-diazine (pyrazine) photodecomposition was thoroughly discussed, no new results have been reported on the photochemistry of this compound in the gas phase. A paper appeared by Suzuka et al.[265] on the spectroscopy of pyrazine in vapor, solutions, and crystal, and another, by Hong and Robinson,[266] on the band assignment in solid-phase spectra. Still unresolved is the discrepancy mentioned by Noyes and Al-Ani[239] between the different triplet yields observed in different laboratories or even those determined by different methods in the same laboratory.[267,268]

2. Dioxanes

The photolysis of gaseous 1,4-dioxane was studied by Hentz and Parrish[269] with radiation of 147.0 nm at 2.7–1.55 Torr at 25–95 °C. The products found were CH_2O, C_2H_4, H_2, and CO with quantum yields that were pressure and temperature independent. The mechanism put forward by the investigators (eq 219a–c) included three primary modes of decomposition of the excited molecule

TABLE XVII. Kinetic Parameters for Thermal Decomposition of 1,3,5-Trioxanes

Compound	Temp range, °C	Log (A/s^{-1})	E_a, kcal/mol	Ref
	297–347	14.80[a]	47.40	272
	272–347	15.0	47.40	274
	209–270	15.13	44.16	273
	215–261	14.38	42.00	275
	215–261	14.79	42.80	275

[a] Corrected from value of 16.16 reported by Burnett and Bell.[272]

$$C_4H_8O_2 \xrightarrow{h\nu} C_4H_8O_2^* \rightarrow C_2H_4 + 2CH_2O \quad (219a)$$

$$\rightarrow C_2H_4 + CH_2O + H_2 + CO \quad (219b)$$

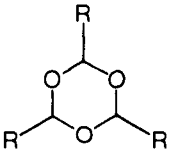
$$\rightarrow H_2 + X \quad (219c)$$

with primary quantum yields $\phi_{219a} = 0.75$, $\phi_{219b} = 0.10$, and $\phi_{219c} = 0.08$. The observation of the invariance of the quantum yield toward temperature and pressure changes, together with previous observation of no gas-phase fluorescence,[270] suggested to Hentz and Parrish[269] that the lifetime of the excited species produced at 147.0 nm was less than 10^{-10} s.

A great difference was found in the product distribution when the 1,4-dioxane was decomposed by excitation with a ruby laser.[271] In this case the main products were C_2H_4, H_2, and CO in relative yields of 1:2:3. A trace of CH_2O was detected. Watson and Parrish[271] were unable to decide whether an excited electronic state was produced in the laser case, or whether a laser-induced pyrolysis was occurring. However the dissociative state must be energetically low lying in either case, and cannot be the state produced by irradiation at 147.0 nm.

C. Trioxolanes

The 1,3,5-trioxolanes are the cyclic trimers of aldehydes. They decompose thermally in a homogeneous first-order reaction to produce the corresponding monomeric aldehydes.



$$\rightarrow 3RCHO \quad (220)$$

The rate parameters for 1,3,5-trioxolane and some alkyl-substituted derivatives are given in Table XVII. Burnett and Bell[272] also examined the decomposition of 2,4,6-trimethyl-1,3,5-trioxolane (paraldehyde) at 261 °C and obtained results in good agreement with those of Coffin.[273]

The 1,3,5-trioxolane itself exhibited the characteristic falloff in rate coefficient at pressures below about 10 Torr at 312 °C[272] and 345 °C.[274] The falloff was not observed for any of the higher homologs under the conditions studied.

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