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Electronic Structure and Gas-Phase Thermolysis of 4-Substituted 3,3,5,5-Tetramethyl-3,5-dihydro-4*H*-pyrazoles Studied by Photoelectron Spectroscopy. First Evidence for an Alkylideneselenirane[1]

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Abstract: The electronic structures of the tetramethyldihydropyrazoles **1** - **5** have been studied by photoelectron spectroscopy and interpreted with the aid of semi-empirical SCF MO calculations (PM3). Gas-phase pyrolyses of **1** - **5** have been carried out and analysed by photoelectron spectroscopy. Both **1** and **2** and in part **3** eliminate molecular nitrogen to form reactive species which cyclize to three-membered rings, i.e. the novel alkylideneselenirane **16**, the alkylidenethiirane *S*-oxide **17**, and the cyclopropanone hydrazone **19**, respectively, which decompose at higher temperatures. The elusive alkylideneselenirane **16** was studied by IR spectroscopy in an argon matrix at 10 K.

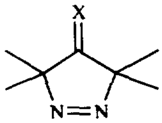
Introduction

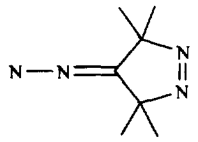
Our previous investigation of the gas-phase pyrolysis of 4-substituted 3,3,5,5-tetramethyl-3,5-dihydropyrazoles (Δ^1-pyrazolines) has uncovered two different routes of thermal decomposition.[2] In both, molecular nitrogen is eliminated with the formation of three-membered rings in a way depending on the nature of the doublebonded substituent at position 4, i. e. either on the least-motion or on the non-least-motion path. The former cyclization leads to ring-contracted molecules with the double bonded substituent unchanged at the three-membered ring; in the products of the latter path, the substituent is part of the three-membered ring. Thus, the course of gas-phase pyrolysis monitored by photoelectron (PE) spectroscopy resembles that of photolysis in solution,[3,4] thermolysis in solution or in the gas-phase in closed vessels,[3,5] and flash vacuum pyrolysis.[6] The thermal extrusion of molecular nitrogen from the parent 4-methylene-Δ^1-pyrazoline has been the subject of a theoretical study.[7]

In continuation of our work on the gas-phase thermolysis of Δ^1-pyrazolines with an exocyclic C=X double bond (X being O, S, CH_2 or NCH_3),[2] we now report the electronic structure and gas-phase pyrolysis of another five tetramethyldihydropyrazoles **1** – **5** (X = Se, S=O, N-NH_2 or N-N=CR_2) using variable temperature PE spectroscopy.[8] Our main purpose is to study the effect of the exocyclic double bond on the mode of cyclization in more detail and to explore further synthetic applications of this reaction.

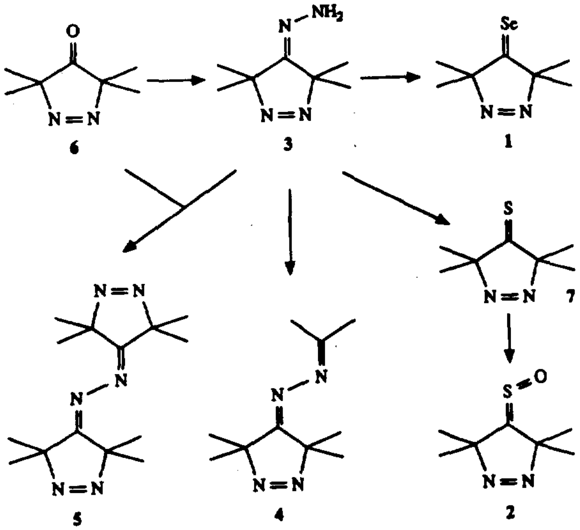
Synthesis of the Tetramethyldihydropyrazoles 1 – 5 and Characterization of the Selone 1

All tetramethyldihydropyrazoles used in this study are derived from the long-known ketone **6**.[4a,9] The hydrazone **3** is converted by the action of dichlorodisulfane in the presence of triethylamine into the thione **7**[4b,10a] which is readily oxidized by peracids to afford the thione *S*-oxide **2**.[10b] Condensation of **3** with acetone and the pyrazolinone **6** yields the unsymmetrical (**4**) and the symmetrical azine (**5**), respectively.



X	Se	S=O	N-NH$_2$	N-N=CMe$_2$	
	1	2	3	4	5

The selone **1** is obtained from the hydrazone **3** by a method developed by Guziec et al.[11] Simultaneous addition of dichloromethane solutions of **3** and dibromodiselane to an excess of triethylamine in the same solvent afforded a blue, volatile oil (47% yield), which furnished the selone **1** as low-melting, deep-blue crystals after flash chromatography. In contrast to di-*tert*-butylselone[12], **1** is oxidized only slowly by atmospheric oxygen.



The blue colour of **1** results from the $n \rightarrow \pi^*$(C=Se) transition, which gives rise to absorptions of low intensity at 696 and 658 nm. The $n^- \rightarrow \pi^*$ transition of the azo chromophor is found in the near UV at 337 nm, while absorptions of high intensity at shorter wavelengths are attributed to the $\pi \rightarrow \pi^*$ (266 nm) and the $n \rightarrow \pi^*$ (217 nm) transition of the selenocarbonyl group, in accordance with the assignments of the UV bands of di-*tert*-butylselone[12,13].

The ^{13}C NMR spectra of **1** are characterized by low-field signals[14] centred at 277.4 ppm ([D$_6$]benzene solution) of the selenocarbonyl carbon atom, e.g. a weak doublet for the ^{77}Se=C group [$^1J(^{77}$Se, ^{13}C) = 224.6 Hz] and a strong singlet for the combinations with the other selenium isotopes which are devoid of a nuclear spin. Further couplings, e.g. $^2J(^{77}$Se,^{13}C) and $^4J(^{77}$Se,^{1}H), were not observed.

The interpretation of the EI mass spectrum of **1** is facilitated by the characteristic isotope pattern of selenium. Extrusion of molecular nitrogen from the molecular ion, followed by loss of a methyl group from the radical ion $C_7H_{12}Se^{+\cdot}$, is the only significant source of ions with *m/z* above 100. Loss of a selenium atom or a SeH radical from $C_7H_{12}Se^{+\cdot}$ gives rise to the formation of ions which may be derived from tetramethylallene (**13**).

Electronic Structure of the Tetramethyldihydropyrazoles 1 – 5

The functional groups N=N and C=X may be regarded as characteristic structural elements of Δ^1-pyrazolines with an exocyclic double bond at C-4. We expect ionization bands arising from these orbitals in the low-energy region of the PE spectra. Previous studies[15] of the electronic structure of Δ^1-pyrazolines have confirmed the natural orbital sequence for the characteristic molecular orbitals of the azo group: n^-_{NN} (HOMO) > $\pi_{N=N}$ > n^+_{NN}. Having an energy of -8 to -12 eV,[15] these orbitals are found in the same region as n_X and $\pi_{C=X}$ (except for X=O, where $\pi_{C=O}$ is extremely low in energy), and we expect a superposition of ionization bands arising from N=N and C=X partial structures. The ionization potentials of a compound which are obtained from PE spectra can be assigned to its molecular orbitals with the aid of semi-empirical quantum chemical calculations on the basis of the Koopmans approximation,[16] $IP(i) \approx -\varepsilon(i)$.

Recorded and calculated (HAM/3) ionization potentials as well as orbital energies (MNDO, 6-31 G) of the tetramethyldihydropyrazolone hydrazone **3** have been published.[15] The PE spectra of compounds **1** – **4** are depicted in Figures 1 and 4 – 6. For the analysis of the spectra, we have used the results of semi-empirical methods (MNDO,[17] AM1,[18] and PM3[19]), the shape of the bands, and the comparison with spectra of similar compounds. Experience revealed PM3 as the most suitable method for the interpretation of the PE spectra of Δ^1-pyrazolines,

Table 1. Vertical ionization potentials IP_v [eV] and orbital energies ε [eV] (PM3) of dihydrotetramethylpyrazoles **1** – **5**.

		n^-_{NN}	n_X	$\pi_{C=X}$	$\pi_{N=N}$	n^+_{NN}
1	IP	8.25	9.16^a	9.92	11.67	11.88
	-ε	10.31	9.43	11.15	12.65	12.95
2	IP	8.96	10.05	9.32^b	11.72	12.05
	-ε	10.02	10.76	9.96^b	12.40	12.61
3	IP	8.72	8.99	10.15^c	11.58	12.01
	-ε	9.84	10.79	9.62^c	12.21	12.50
4	IP	8.25	9.08^d	9.28^e	11.49	12.10
	-ε	10.06	9.47^d	10.06^e	12.09	12.43
5	IP	8.24, 8.74	9.30^d	9.50^e	11.31	11.77
	-ε	9.67, 10.09	10.46^d	10.66^e	12.34	12.64

^{a} Vibrational splitting: 1600 cm^{-1}. ^{b} π_2(CSO). ^{c} π_2(CNN). ^{d} n^+_{NN}(azine). ^{e} π_2(azine).

hence MNDO and AM1 results were omitted in the present paper. Orbital energies, as calculated by PM3, and the ionization potentials of compounds **1** – **5** are given in Table 1.

The PE spectrum of the selone **1** strongly resembles that of tetramethyldihydropyrazolethione **7**[2], apart from a shift to lower IPs of all bands, which arises from the replacement of sulfur by its higher homologue selenium (Figure 2). Accordingly, the assignment for the thione **7**[15] has been adopted for **1** despite of a different orbital sequence predicted by the calculations.

The oxidation at the sulfur atom of thione **7** leads to a weakening of the C=S double bond. Calculations show an antibonding combination of $\pi_{C=S}$ and n_O and, therefore, a destabilization of the corresponding molecular orbital in the thione *S*-oxide **2**. This is why the second band in the PE spectrum of **2** is that arising from the ionization from a π orbital rather than from an n orbital, as is usually the case. The third band is due to the ionization from the orbital n_S. This sequence for the thione *S*-oxide **2** is confirmed by the comparison of the second and the third band with the first two bands of thioformaldehyde *S*-oxide, the parent sulfine, which exhibit similar structures.[20] The electronic structure of the C=S=O moiety is also of significant relevance for its reactivity in 1,3-dipolar cycloadditions.[21]

The assignment of the PE spectrum of hydrazone **3** has been carried out through comparison with that of acetone hydrazone [IP: 8.74 eV n_N, 9.97 eV π_2(CNN)]. The introduction of an azo group into this molecule shifts the first two bands towards higher ionization potentials. In front of these two bands, the typically broad band arising from an n^-_{NN} ionization is observed. This assignment is in accord with the previous one.[15]

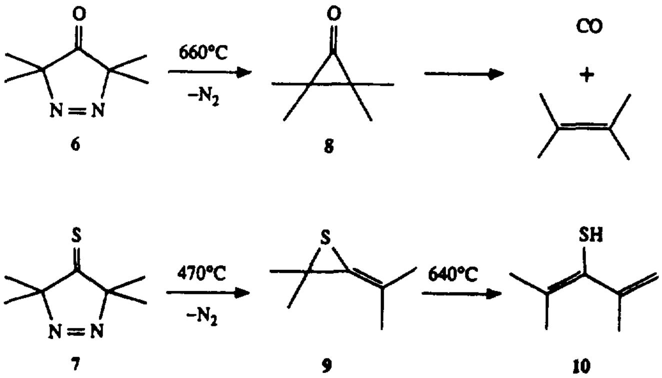
For the analysis of the electronic structure of the azines **4** and **5**, the PE spectrum of acetone azine[22] (IP: 8.48 eV n^+, 9.08 eV π_2) is used as a reference. The second C=N double bond of the azine moiety causes a splitting of n and π orbitals. The energies of the newly formed orbitals n^+ and π_2 are raised. Again, stabilization of both orbitals is achieved through the combination with the orbitals of the azo group(s). With regard to the azo group, the symmetrical azine **5** represents a special case. Because **5** is the formal dimer of a 4-iminylpyrazoline radical, all orbitals of the pyrazoline ring are found twice, namely in the symmetrical (s) and the antisymmetrical (a) combination relative to the C_2 axis. In the PE spectrum of **5**, we observe two bands in front of the n-π double band. Both bands exhibit the characteristic n^-_{NN} shape and differ in energy as predicted by the calculations.

Whereas the energies of the orbitals n^+_{NN} and $\pi_{N=N}$ of all Δ^1-pyrazolines having an exocyclic double bond at C-4 seem to be approximately constant, that of n^-_{NN} varies over a wide range. The most striking discovery is the large stabilization by 0.4 eV of this orbital in the thione *S*-oxide **2**, for which mainly inductive effects must be responsible. MO calculations show that in **2** n^-_{NN} interacts with σ MOs of the C=S=O group.

Thermolysis of the Tetramethyldihydropyrazoles 1 – 5

The gas-phase thermolyses of compounds **1** – **5** were carried out at low pressure (50 Pa) in the PE spectrometer and monitored by real-time gas analysis.[8] This technique allows detection of intermediates (half-lifes as short as ≈0.1 s) as well as stable products. Because the dinitrogen molecule is preformed in the Δ^1-pyrazolines, their decomposition always involves its loss and hence can be studied by following the appearance of the sharp peaks of molecular nitrogen (15.60, 16.98, 18.78 eV).[23]

By analogy with the gas-phase pyrolyses of tetramethyldihydropyrazolone **6** and the thione **7**,[2] which afford the least-motion (**8**) or the non-least-motion product **9**, one of two possible three-membered rings may be anticipated. Bands belonging to such three-membered ring products are expected to appear in the PE spectra obtained at intermediate temperatures. Higher temperatures may give rise to secondary products by rearrangements, e.g. **10**, or cheletropic decomposition of the heteromethylenecyclopropanes.



6 **8** **7** **9** **10**

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazole-4-selone (1)

A search for the intriguing alkylideneselenirane **16** starting from **1** has been carried out in solution.[24] Because only a small number of stable selenoketones exist, studies of their decomposition are scarce. Irradiation of di-*tert*-alkylselones with UV light in hydrogen-donating solvents affords diselenides,[13] and the selone **1** behaves likewise yielding **12** which subsequently loses selenium to produce **11** in a manner closely resembling the photodecomposition of other diselenides.[13] A second path of photolysis involves extrusion of molecular nitrogen from **1** to yield eventually tetramethylallene (**13**) and elemental selenium, probably via the elusive alkylideneselenirane **16**. This hypothesis is corroborated by the observation of additional products which are derived from the dieneselenole **14**. Heating a solution of **1** in $[D_6]$benzene to 120°C leads to a similar mixture of products, except that dimethylpentadiene **15**, which apparently arises from **13** by an acid-catalyzed rearrangement, predominates.[25] Thus, attempts to observe the alkylideneselenirane **16** in solution have been frustrated by its instability in the condensed phase.[24]

The photochemical properties of selenoketones resemble those of thioketones rather than ketones.[13] This also holds for the electronic structures as discussed above. Therefore, it was not surprising to observe an analogy between the gas-phase pyrolysis of selone **1** (Figure 1) and that of the corresponding thione **7**.[2] In both cases, three steps can be distinguished: At 350 °C, the elimination of molecular nitrogen from **1** leads to the non-least-motion product. i.e. the novel isopropylideneselenirane **16** (7.73, 9.50, 9.74, 10.34 eV).[26] Surprisingly, **16** does not loose selenium[27] at 750 °C but rearranges to form the selenole **14** (8.19, 9.22, 9.93, 11.00 eV) which decomposes into hydrogen selenide (9.91 eV[28]) and unidentified products at 1100 °C.

We interpret the PE spectra of **14** and **16** by comparing them with those of the corresponding sulfur compounds, e.g. dimethylpentadienethiol **10** and isopropylidenedimethylthiirane **9**,[2] and with the aid of semi-empirical calculations. Figure 2 shows the first ionization potentials observed in the PE spectra of hydrogen sulfide and known sulfur compounds, hydrogen selenide and the as yet unknown selenium analogues **1**, **14**, and **16**.

On passing from a sulfur compound to the selenium homologue, ionizations are lowered. Those arising from molecular orbitals localized at the heteroatoms are most strongly affected. This can be observed in the shifts between the n_X ionization of hydrogen sulfide and selenide (0.7 eV), the pyrazolines **7** and **1** (second

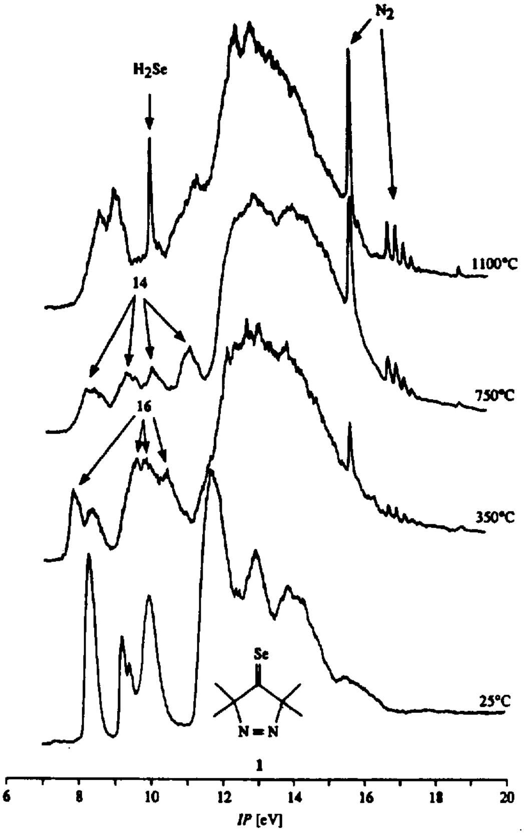
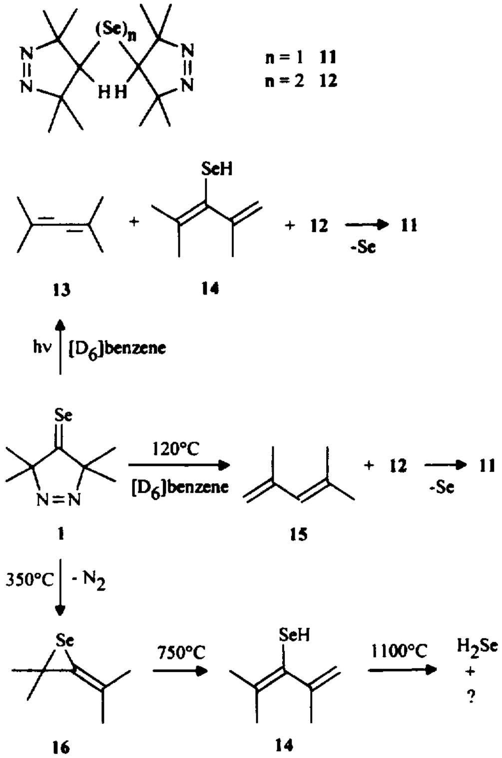


Figure 1. Photoelectron spectra of the dihydropyrazoleselone **1** recorded at 25, 350, 750, and 1100 °C.



band, 0.2 eV), and the dienes **10** and **14** (third band, 0.5 eV), and also in the lowering of the $\pi_{C=X}$ ionization of the pyrazolines **7** and **1** (0.5 eV). The other high-energy orbitals possess either only a small wavefunction coefficient at the heteroatoms or none. Accordingly, the ionization potentials are either lowered by only about 0.1 eV or not at all. In both heterocyclopropanes **9** and **16**, each of the four highest occupied molecular orbitals, the π MOs π_2(CCX) and π_1(CCX), and the Walsh orbitals ω_S and ω_A (in the order of increasing ionization potentials) has electron density at the heteroatom. Therefore, each ionization potential is lowered, the shifts ranging from 0.2 eV [π_2(CCX)] to 0.5 eV (ω_S).

As an independent structural proof for the selenirane **16**, we have studied it by IR spectroscopy at low temperature in an argon matrix.[29] In this experiment, **16** was generated from **1** by photolysis in the matrix and by gas-phase thermolysis at temperatures between 350 and 800 °C. IR spectra of trapped **16** (Figure 3) were recorded at 10 K. The observed frequencies and intensities of **16** are in good agreement with those obtained by ab initio calculations (Gaussian 94, basis set LanL2DZ).[30] As expected, the IR spectrum of **16** resembles that of the thiirane **9**. A full report of the matrix study, together with that of the analogous oxygen and sulfur compounds, will follow.

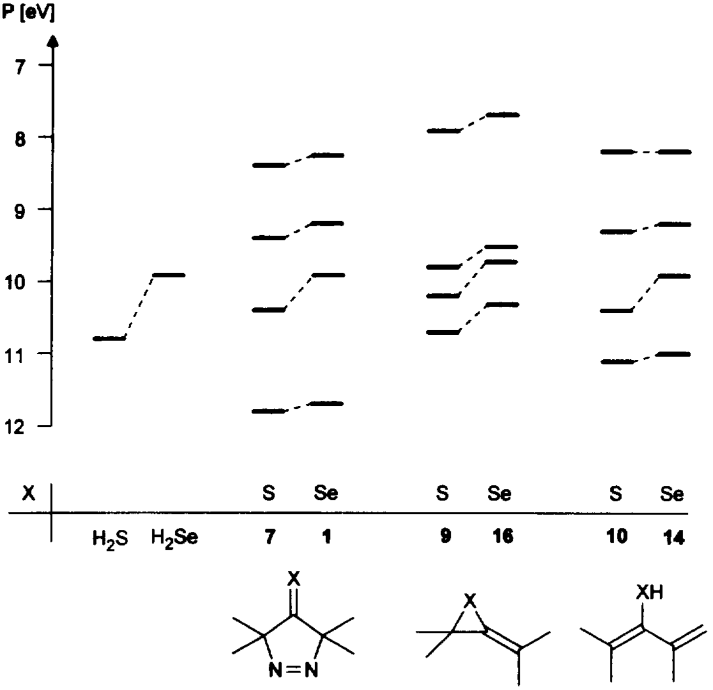


Figure 2. Correlation of the first ionization potentials of hydrogen selenide, the dihydropyrazoleselone **1**, the isopropylideneselenirane **16**, and the dieneselenole **14** with those of the corresponding sulfur compounds.

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazole-4-thione S-oxide (2)

Irradiation of **2** in [D$_6$]benzene solution with light of wavelengths above 320 nm affords predominantly tetramethylallene (**13**) and tetramethylpyrazolinone **6** (3 : 2) together with small amounts of a third product characterized by a 2,4-dimethylpenta-1,3-dien-3-yl moiety as shown by the ^{1}H and ^{13}C NMR spectra.[24] The photolysis of similar pyrazoline thione *S*-oxides in solution has been investigated by Schaumann et al.,[22] who have studied compounds bearing two methyl groups at C-5 and two tertiary alkyl groups at C-3 of the pyrazoline ring. These pyrazoline thione *S*-oxides are reported to loose nitrogen to form alkylidenethiirane *S*-oxides in low yields. On thermolysis, thiirane *S*-oxides are known to eliminate sulfur monoxide which is highly unstable and eventually yields sulfur dioxide.[31] Other thione *S*-oxides, including the parent sulfine, thioformaldehyde *S*-oxide, decompose via intermediate oxathiiranes which eliminate elemental sulfur to produce the corresponding aldehyde or ketone.[32,33] This mechanism accounts for the formation of **6** in the photolysis of **2**. The results of recent ab initio calculations at the MP-2 level by Block, Schwan and Dixon[34] show that **17** and **18** are essentially isoenergetic, **17** being more stable than **18** by as little as 0.4 kcal/mol after zero-point corrections. The first ionization potential (HOMO energy) was predicted to be 9.07 eV for **17** and 9.42 eV for **18**.

The PE spectra recorded during pyrolysis of thione *S*-oxide **2** (Figure 4) show that the decomposition occurs in two steps. The expected band of sulfur dioxide (12.64 eV) is observed at 700 °C. A difference of 0.14 eV to its literature value of 12.50 eV[23] is found. Ionization bands belonging to sulfur monoxide (10.31, 13.81 eV[35]) cannot be detected. In the low-energy region, bands are observed at 8.52 and 9.00 eV which exhibit the typical structure

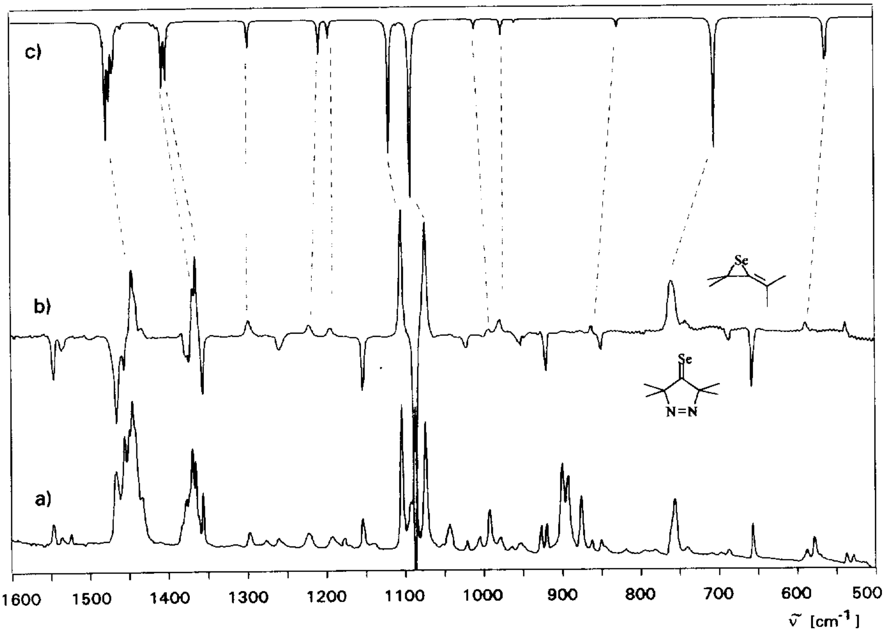


Figure 3. IR spectra showing the photolysis and flash vacuum pyrolysis (FVP) of dihydropyrazoleselone **1**:

(a) FVP (800 °C) of **1** with subsequent trapping of the products in argon at 10 K. The IR spectrum indicates a 2:1-mixture of **16** and **1**.

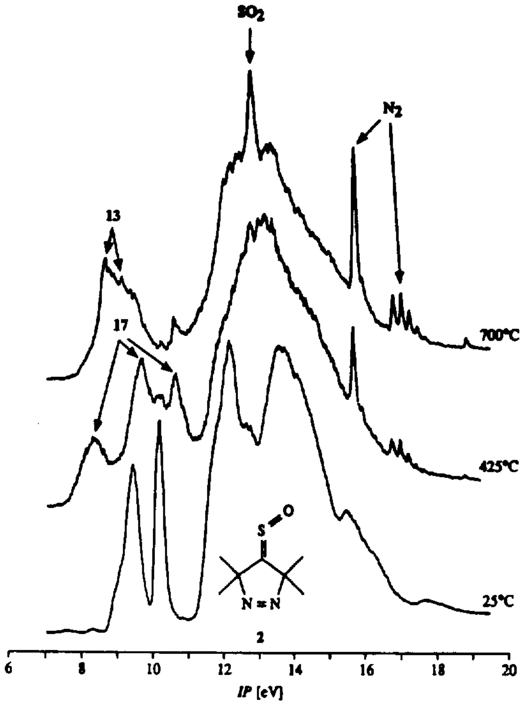
(b) Difference spectrum showing the photolysis of **1** ($\lambda > 320$ nm, argon matrix at 10 K). Bands pointing downwards are disappearing during the photolysis and assigned to **1**. Bands pointing upwards are appearing during photolysis and assigned to selenirane **16**.

(c) Ab initio calculated IR spectrum of selenirane **16** using the LanL2DZ[30b)] basis set. The frequencies were scaled by 0.9 to allow the direct comparison with the experimental spectrum, and a Lorentz band shape was simulated with a half-value width of 2 cm^{-1}.

of those of allenes and belong to tetramethylallene (**13**).[36] This is the expected product for loss of sulfur monoxide from the alkylidenethiirane *S*-oxide **17**, which may result from the extrusion of dinitrogen from the sulfine **2**. Therefore, we assign the bands at 8.25, 9.57, and 10.52 eV in the PE spectrum taken at 425 °C to **17**. The alternative primary product in the pyrolysis of **2** would be the tetramethylcyclopropanethione *S*-oxide (**18**). This hypothetical species is expected to decompose into sulfur and tetramethylcyclopropanone (**8**) and hence should result in the same pyrolysis PE spectrum as tetramethyldihydropyrazolone **6**,[2] the most prominent feature of which (except for the bands of molecular nitrogen) is the ionization band of carbon monoxide at 14.01 eV.[23] Because this band is missing in the high-temperature pyrolysis PE spectrum of **2**, the intervention of **8** and, therefore, **18** is excluded.

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazol-4-one hydrazone (3)

Because the gas-phase pyrolysis of simple hydrazones has not yet been investigated by real-time gas analysis, we have studied the thermal decomposition of acetone hydrazone as a model for **3**. Changes in the PE spectrum can-



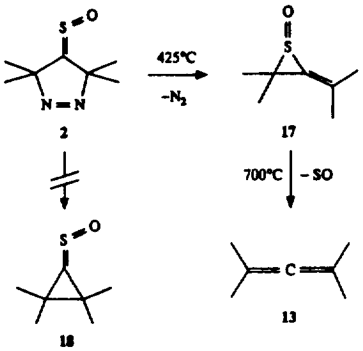


Figure 4. Photoelectron spectra of the dihydropyrazolethione S-oxide 2 recorded at 25, 425, and 700 °C.

not be detected before a temperature of 625 °C has been reached when bands of acetonitrile (12.21, 12.45, 13.16 eV[23]) and ammonia (10.8 eV[28]) appear. As the temperature is increased, these bands become more intense and additional bands arising from the methyl radical (9.87 eV[37]), hydrogen cyanide (13.63, 13.84 eV[23]) and molecular nitrogen (15.60 eV[23]) emerge. At 825 °C, the highest temperature applied, the pyrolysis is still incomplete. The appearance of ammonia and dinitrogen indicates the disproportionation of the NH_2 radical formed by breaking the N-N bond. In an attempt to uncover the source of hydrogen cyanide, we tried to pyrolyse acetonitrile. Because we were unable to detect any bands arising from hydrogen cyanide, it cannot be formed from acetonitrile. Therefore, hydrogen cyanide may originate from both NH_2 and NH_3 which are known to react in this way with various organic compounds.[38]

The PE spectrum recorded during pyrolysis of 3 at 850 °C (Figure 5, Scheme 3) shows bands of the expected products, i.e. molecular nitrogen, ammonia, and hydrogen cyanide. Furthermore, a band at 12.87 eV is observed and assigned to methacrylonitrile (**20**) whose other bands (10.38 and 10.57 eV) are superimposed with those of ammonia. In addition, propene is produced which gives rise to the ionization peaks at 9.75 and 9.97 eV (IP_a 9.73 eV,[39] IP_v 10.03 eV[23]). Finally, the band at 8.50 eV is assigned to the first ionization of 2,3-dimethyl-

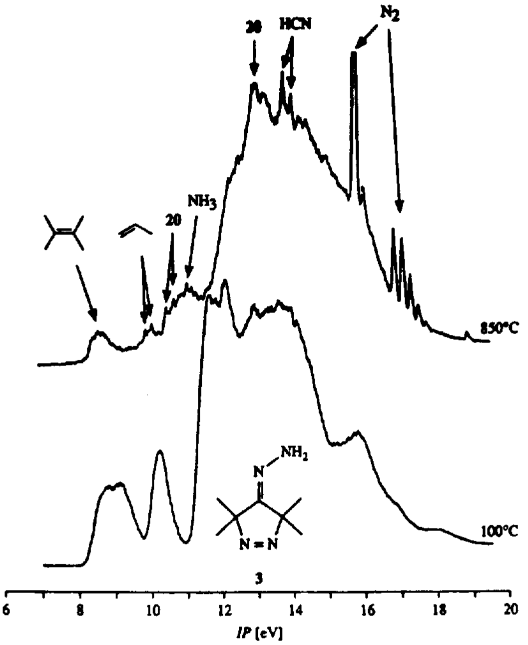
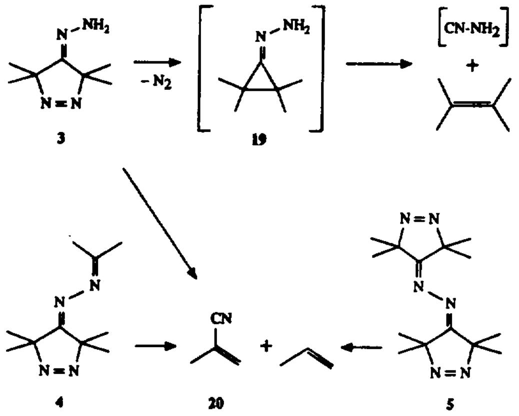


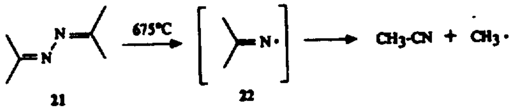
Figure 5. Photoelectron spectra of the dihydropyrazolone hydrazone 3 recorded at 100 and 850 °C.



2-butene, the formation of which can be rationalized in terms of the extrusion of molecular nitrogen to yield tetramethylcyclopropanone hydrazone 19[40] and its subsequent cheletropic decomposition. The latter mode of pyrolysis closely resembles that of 4-methylimino-3,3,5,5-tetramethyl-3,5-dihydro-4*H*-pyrazole[2] while the former (leading to 20 and propene) is also found for the azines 4 and 5 (see below).

Azines 4 and 5

In order to obtain a guidance for the interpretation of the pyrolyses of 4 and 5, we have studied that of acetone azine (21). At a temperature of 675 °C, acetonitrile[23] is the only stable product. In addition, the band of the methyl radical is oberved at 9.85 eV.[37] This result confirms the expected breaking of the N-N bond to give two iminyl radicals 22 as the primary intermediates.



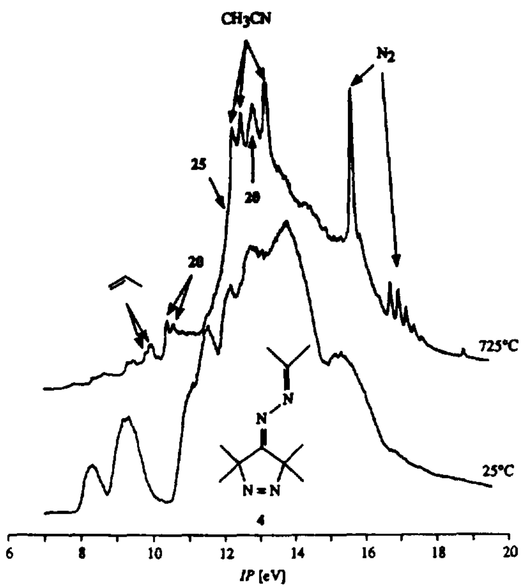
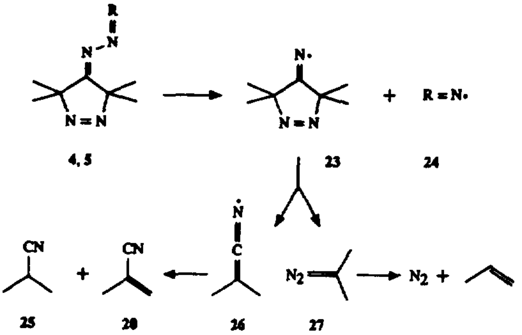


Figure 6. Photoelectron spectra of the unsymmetrical azine 4 recorded at 25 and 725 °C.



As acetone azine (21) and 4 have the -N=CMe$_2$ moiety in common, formation of acetonitrile and the methyl radical is also expected in the pyrolysis of 4. The elimination of molecular nitrogen commences at a temperature of 450 °C and is complete at 725 °C (Figure 6, Scheme 4). Besides the bands of acetonitrile[23] and the methyl radical,[37] the ionizations of propene[23,39] are found. Further bands are detected at 10.36, 10.53, and 12.84 eV, which are assigned to methacrylonitrile (20). A shoulder at 11.9 eV indicates the presence of isobutyronitrile (25). As a result of superposition of several ionizations, a complex band is observed at about 10 eV, which has been commented on in the literature.[41] We note that neither significant amounts of 2,3-dimethyl-2-butene, which might have indicated the intervention of the unsymmetrical acetone tetramethylcyclopropanone azine, nor any possible intermediates emerge: The product bands appear as the bands of 4 vanish.

Irradiation of a degassed [D$_6$]benzene solution of 5 at 90 °C slowly affords a mixture of 2,3-dimethyl-2-butene and tetramethylsuccinodinitrile (9 : 1 at 20% conversion) in almost quantitative yield together with molecular nitrogen and traces of isobutyronitrile.[24,42] The two nitriles are probably formed by dimerization and disproportionation of the α-cyanoisopropyl radical (26), respectively. This species is generated, along with 2-diazopropane (27), from the iminyl radical 23 resulting from cleavage of the N-N bond.[43] 2,3-Dimethyl-2-butene, on the other hand, is indicative of cheletropic decompositions of tetramethylcyclopropanone azine type intermediates.

Thermal decomposition of 5 in the gas-phase pyrolysis commences at a temperature of 400 °C, when the characteristic bands of molecular nitrogen appear. As in the pyrolysis of azine 4, there is no indication of intermediates. The products of 5 are predicted on the basis of the pyrolysis of 4, because the fragments arising from the pyrazoline moiety of both 4 and 5 are identical. At a temperature of 1050 °C, ionization bands are observed, which are assigned to methacrylonitrile (**20**) (10.35, 10.51, and 12.88 eV), isobutyronitrile (**25**) (11.89 eV), and propene. Even at temperatures as high as 1050 °C, the decomposition of **5** is not complete as its bands are still present in the spectrum. The high thermal stability of **5** parallels its reluctance to undergo photodecomposition.[24,42]

The primary process in the pyrolysis of azines **4**, **5**, and **21** is the cleavage of the N-N bond which is followed by the decay of the iminyl radicals **22**, **23**, and **24** (= **22** or **23**) thus formed. The iminyl radical **23** may undergo [3+2] cycloreversion of the dihydropyrazole ring to afford 2-diazopropane (**27**) and the α-cyanoisopropyl radical (**26**), the precursor of methacrylonitrile (**20**) and isobutyronitrile (**25**). In fact, **26** has been observed by PE spectroscopy in the 370 °C flash vacuum pyrolysis of azodiisobutyronitrile.[44] Dimerization of **26** at this temperature yielded tetramethylsuccinodinitrile while peaks due to **20** and **25** were found at higher temperature. Furthermore, the intermediate occurrence of **26** is supported by the formation of tetramethylsuccinodinitrile[45] on photolysis of **5** in solution.[42] Finally, molecular nitrogen and propene are the products of the well-known thermal decomposition of **27**.

Conclusion

The extrusion of molecular nitrogen is the first observable step in the gas-phase thermolysis of the 4-substituted tetramethyldihydropyrazoles **1** – **5** of the present study and of **6** and **7** as well.[2] While delineation of the details of this process is beyond the limits of the method employed, the gross mode of formation of nitrogen seems unambiguous in those thermolyses that yield products possessing six or seven carbon atoms as is true for **1** – **3**, **6**, and **7** but not for the azines **4** and **5**. These products are heteromethylenecyclopropanes (**8**, **9**,[2] **16**, and **17**) or are derived therefrom (i.e. **10**, **13** – **15**, and 2,3-dimethyl-2-butene). The heteromethylenecyclopropanes are generated on the least-motion or the non-least-motion path. The former is followed if the hypothetical primary intermediates can cyclize to yield tetramethylcyclopropanone (**8**), its hydrazone **19**, and the corresponding N-methyl imine,[2] whereas the latter is preferred if the alkylidenethiirane **9**, the corresponding *S*-oxide **17**, and the novel alkylideneselenirane **16** result. Thus, those three-membered ring systems that are predicted by quantum chemical calculations to be lower in energy[34,46] are indeed formed.

The pyrolyses of the azines **4** and **5** appear to take a fundamentally different route as indicated by the absence of tetramethylcyclopropane-derived products. Cleavage of the N-N bond is the primary process which is followed by the decay of the iminyl radicals thus formed.

In the thermolysis of the hydrazone **3**, both pathways may be invoked to account for the products, i.e. the one involving N-N cleavage and the route via tetramethylcyclopropanone hydrazone (**19**).

Experimental

PE spectra were recorded on a Leybold-Heraeus UPG 200 spectrometer with He(I) excitation (21.21 eV). Spectra were calibrated with lines of xenon (12.13 and 13.44 eV) and argon (15.76 and 15.94 eV). The accuracy of the ionization potentials is ± 0.03 eV for sharp peaks and ± 0.05 eV for broad and overlapping signals.

Thermolyses were carried out in a heated molybdenum tube (80 mm length, 4.5 mm inner diameter) placed between sample inlet and ionization chamber in the PE spectrometer. The distance between the molybdenum tube and ionization chamber was about 35 mm. Temperatures are accurate to ± 5 °C.

IR spectra: Perkin-Elmer spectrometer 1420 and 1600. UV spectra were recorded from solutions in hexane on a Hitachi UV/Vis spectrometer U 3200. NMR spectra were taken from solutions in $CDCl_3$ on a Bruker spectrometer WM 400. Mass spectra (70 eV) were run on a Finnigan MAT mass spectrometer 8200. Melting points were taken in sealed capillary tubes on an apparatus from Büchi, Flawil, Switzerland.

Matrix spectroscopy: Matrix isolation experiments were performed by standard techniques[47] with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) at 30 K on a CsI (IR) window at a rate of approximately 0.15 mmol/min. IR spectra were measured in the range of 400 - 4000 cm^{-1} by using a Bruker IFS 66 FTIR spectrometer with a standard resolution of 1 cm^{-1}. Irradiations were carried out with Osram HBO 500-W mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water. For broad-band irradiation, Schott cut-off filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors ("cold mirrors") and cutoff filters were employed.

Calculations were performed with the MOPAC program package (version 6.1)[48] and with the program Gaussian 94.[30]

Dibromo diselenide[11] and the pyrazolines **2**,[10b] **3**,[4b,9,10b] and **6**[5b] were prepared as described in the literature.

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazole-4-selone (1). A solution of hydrazone **3** (1.54 g, 10 mmol) in dry dichloromethane (30 ml) and a solution of dibromo diselenide (6.36 g, 20 mmol) in the same solvent (30 ml) were added simultaneously dropwise to a stirred solution of triethylamine (3.04 g, 30 mmol) in dichloromethane (40 ml) kept at 0 °C under a nitrogen atmosphere. The mixture was stirred for 30 min at room temperature and worked up as quickly as possible. The precipitate (red selenium and triethylammonium bromide) was removed by filtration through a narrow-porous glass sinter funnel and washed with little dichloromethane. The filtrate and washings were combined and extracted with water (50 ml) which was extracted in return with dichloromethane (50 ml). The combined organic layers were rapidly filtered through a pad of potassium carbonate (5 g) and dried with sodium sulfate. After distillation of the solvent in vacuo, the brown residue was cautiously distilled in a short-path apparatus at 10 Torr with the aid of a heatgun while the resulting blue oil (0.95 g, 47%) was condensed at -78 °C. Immediate flash chromatography on silica [32 – 63 μm, ICN Biomedicals, (40 x 4)-cm column] with petroleum ether (30 – 50 °C)/ethyl acetate (98:2) yielded deep-blue crystals (0.63 g, 31%), m. p. 46 – 48 °C, which were stored under nitrogen at -20 °C in the dark. – IR (CCl_4): 1465, 1380, 1360, 1150, 1085 cm^{-1}. – UV, λ_{max} (log ε): 217 (3.577) [$n\rightarrow\sigma^*$(C=Se)], 266 (3.908) [$\pi\rightarrow\pi^*$(C=Se)], 337 (2.480) [$n^-\rightarrow\pi^*$(N=N)], 658 (1.316), 696 nm (1.365) [($n\rightarrow\pi^*$(C=Se)]. – ^1H NMR: 1.54 ppm (s); (C_6D_6): 1.28 ppm. – ^{13}C NMR: 25.7 (CH_3), 106.7 (quart. C), 279.2 [s and d, $^1J(^{77}Se,^{13}C) = 224.6$ Hz, (C=Se)]. – ^{77}Se NMR (C_6D_6): 1898.0 ppm (standard Me_2Se). – MS, *m/z* (%) (^{80}Se peaks): 204 (4) [M^+], 176 (13) [$M^+ - N_2$], 161 (38) [$M^+ - N_2 - CH_3$], 95 (28) [$C_7H_{11}^+$], 81 (25) [$C_6H_9^+$], 79 (42), 77 (28), 67 (100), 55 (85), 53 (57), 41 (71).

3,3,5,5-Tetramethyl-4-(3-methyl-1,2-diaza-2-butenylidene)-3,5-dihydro-4H-pyrazole (4). A solution of hydrazone **3** (1.54 g, 10 mmol) in acetone (25 ml) containing 1 drop of acetic acid was heated under reflux for 2 h. The cold solution was filtered through potassium carbonate which was eluted with dichloromethane (3 x 50 ml). Distillation of the solvent in vacuo and sublimation of the residue at 30 °C/10^{-3} Torr yielded colourless crystals (1.78 g, 92%), m. p. 43 – 44 °C. – IR (KBr): 1661, 1617 (C=N), 1544 cm^{-1} (N=N). – UV, λ_{max} (log ε): 220 (4.152), 336 nm (2.614) $[n^- \rightarrow \pi^*(N{=}N)]$. – ^1H NMR: 1.51 (2 CH_3), 1.53 (2 CH_3), 1.87 (CH_3), 2.03 (CH_3). – ^{13}C NMR: 17.8 (CH_3), 22.3 (CH_3), 24.9 (CH_3), 25.7 (CH_3), 85.3 (quart. C), 86.6 (quart. C), 162.0 (C=N), 171.3 (C=N). – MS: *m/z* (%): 194 (5) $[M^+]$, 166 (54) $[M^+ - N_2]$, 151 (29) $[M^+ - N_2 - CH_3]$, 139 (15), 123 (16), 109 (54), 97 (100), 82 (7), 68 (29). – Calc. for $C_{10}H_{18}N_4$ (194.28): C, 61.82; H, 9.34; N, 28.83%. Found: C, 61.12; H, 9.27; N, 27.89%.

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazol-4-one azine (5). A mixture of ketone **6** (14.0 g, 100 mmol), hydrazone **3** (15.4 g, 100 mmol), and acetic acid (1 ml) was heated in a closed flask to 110 °C for 48 h. The mixture, which was a liquid at the beginning, crystallized during 28 h. Recrystallization of the product from ethyl acetate/ethanol afforded pale yellow crystals (19.9 g, 72%), m. p. 160 °C, which were recrystallized from toluene at -20 °C to yield colourless crystals (15.7 g), m. p. 163 – 164 °C. – IR (KBr): 1667 (C=N), 1544 cm^{-1} (N=N). – UV: λ_{max} (logε): 216 (4.266), 223 (4.279), 336 nm (2.705) $[n^- \rightarrow \pi^*(N{=}N)]$. – ^1H NMR: 1.52 (s), 1.59 ppm (s). – ^{13}C NMR: 22.8 (CH_3), 25.4 (CH_3), 85.8 (quart. C), 86.8 (quart. C), 176.1 ppm (C=N). – MS: *m/z* (%): 276 (4) $[M^+]$, 248 (4) $[M^+ - N_2]$, 220 (10) $[M^+ - 2N_2]$, 111 (82), 96 (57), 81 (100), 41 (89). – Calc. for $C_{14}H_{24}N_6$ (276.4): C, 60.84; H, 8.75; N, 30.41%. Found: C, 60.90; H, 8.72; N, 30.63%.

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