Gas-Phase Thermolysis of 4-Substituted 3,5-Dihydro-3,3,5,5-tetramethyl-4H-pyrazoles Studied by Photoelectron Spectroscopy and Flash Vacuum Pyrolysis

Markus K. Kindermann[a], **Rainer Poppek**[a], **Paul Rademacher**[a]*, **Andreas Fuß**[b], and **Helmut Quast**[b]*

Institut für Organische Chemie der Universität-GHS Essen[a],
Universitätsstraße 5—7, D-4300 Essen 1

Institut für Organische Chemie der Universität Würzburg[b],
Am Hubland, D-8700 Würzburg

Gas-phase thermolyses of the 3,5-dihydro-4H-pyrazoles **1—4** have been studied by photoelectron spectroscopy and flash vacuum pyrolysis. In the PE-controlled thermolysis, **1—4** extrude molecular nitrogen, and the fragments cyclize immediately to different three-membered rings. In the case of **2** and **3**, the former 4-substituent becomes part of the three-membered ring, whereas **1** and **4** afford short living oxo- and iminocyclopropanes. At higher temperatures and in flash vacuum pyrolysis, acyclic compounds and smaller molecules are formed in a second step. Based on MNDO, AM1, and PM3 calculations, the ionization potentials of 3,5-dihydro-3,3,5,5-tetramethyl-4-methylene-4H-pyrazole (**3**) have been assigned to molecular orbitals. To aid the identification of the pyrolysis products, PE spectra of the methylenethiirane **9** and the methylenecyclopropanes **11** and **13** have been measured and interpreted with the aid of SCF calculations.

3,5-Dihydro-4H-pyrazoles (Δ^1-pyrazolines) are interesting compounds because intriguing diradicals may be formed as intermediates of their photochemical and thermal decomposition[1]. In particular, 3,5-dihydro-4-methylene-4H-pyrazole is a well-known precursor of the trimethylenemethane diradical, which may exist in several geometries, spin states, and electronic states, the lowest being the planar triplet state[2]. In continuation of our work on the thermolysis of heterocycles containing vicinal nitrogen atoms[3], we have investigated the variable-temperature photoelectron spectroscopy[4,5] and flash vacuum pyrolysis[6] of the 4-substituted 3,5-dihydro-3,3,5,5-tetramethyl-4H-pyrazoles **1—4**.

obtained from photoelectron (PE) spectra with molecular orbital energies. The PE spectrum of **1** has been measured by Houk et al.[9], and the PE spectra of **2** and **4** have been published recently by Gleiter, Veszprémi, and Quast[10]. We have performed some additional MO calculations using the MNDO[11], AM1[12], and PM3[13] method to confirm the interpretation of these data. The PE spectrum of the methylene compound **3** (see Figure 1) has now been analyzed in the same way as the other compounds of this series. The ionization potentials and the energy values of some important molecular orbitals are listed in Table 1.

	X
1	O
2	S
3	CH_2
4	$N-CH_3$
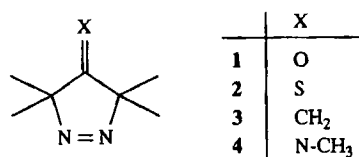
Electronic Structures of the 3,5-Dihydro-3,3,5,5-tetramethyl-4H-pyrazoles 1—4

The 3,5-dihydro-3,3,5,5-tetramethyl-4H-pyrazoles **1—4** may be considered as a combination of an exocyclic double bond with a cis-azo group in a five-membered ring. The four methyl groups prevent tautomerization to 1,5-dihydro-4H-pyrazoles (Δ^2-pyrazolines), which plagues studies of lower homologs. Because of the three sp^2-hybridized ring atoms and the four methyl groups, such a five-membered ring is expected to be almost planar[7].

The Koopmans approximation[8], $IP(i) \approx -\varepsilon(i)$, allows the correlation of the ionization potentials which can be
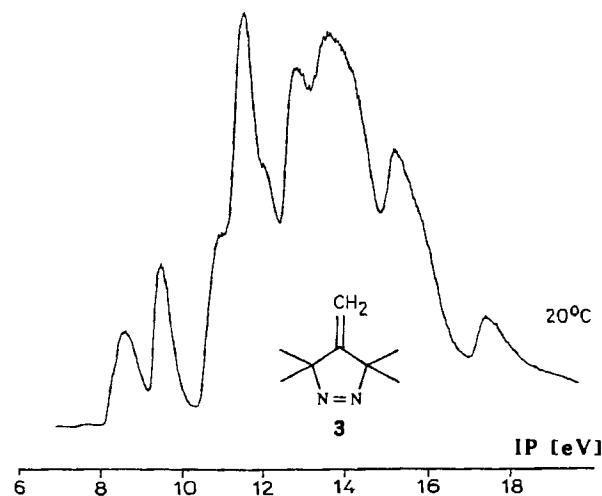
Figure 1. PE spectrum of 3,5-dihydro-3,3,5,5-tetramethyl-4-methylene-4H-pyrazole (**3**)

Table 1. Vertical ionization potentials I_v [eV] and calculated orbital energies ε [eV] of the 3,5-dihydro-4-methylene-4H-pyrazole 3

Band	I_v	Assignment	$-ε$ (MNDO)	$-ε$ (AM1)	$-ε$ (PM3)
1	8.63	n^-_{NN}	10.61	10.26	9.79
2	9.56	$π_{CC}$	10.35	10.32	10.59
3	11.00	$π_{NN}$	12.47	12.16	12.25
4	11.64	n^+_{NN}	12.97	12.54	12.37
5	12.04	$σ_{CC}$	12.10	11.40	11.96
6	12.86				
7	13.64				
8	15.28				

The assignment of the PE spectrum of 3 follows the interpretation of the PE spectra of 1, 2, and 4[9, 10]. As may be seen from Table 1, the calculated data do *not* agree with the experimental results as far as the MO sequence is concerned. In the case of 1, 2, and 4, the MNDO calculations indicate that the electron lone pairs of the 4-substituents (n_O, n_S, n_N) occupy the highest occupied orbitals. This is in contrast to the interpretation based on vibrational fine structure and band shapes which assigns the lowest ionization potentials to the n^-_{NN} orbitals[9, 10]. The same holds true for the methylene compound 3 (Table 1). The ionizations from the molecular orbitals $π_{NN}$ and n^+_{NN} were assigned by comparison with the corresponding ionization potentials of similar compounds (e.g. 1, 2, 4, and 3,5-dihydro-3,3,5,5-tetramethyl-4H-pyrazole[9, 10]), because the respective ionization energies are approximately constant. Only the second ionization potential (9.56 eV) remains unassigned, and we attribute it to the $π_{CC}$ orbital, which typically occurs in this region[14]. The complete assignment is in accordance with the AM1 and PM3 calculations, except that a $σ_{CC}$ orbital was calculated as the third highest occupied molecular orbital.

Thermolysis of the 3,5-Dihydro-3,3,5,5-tetramethyl-4H-pyrazoles 1−4 in the Photoelectron Spectrometer

The planar five-membered ring of the 3,5-dihydro-4H-pyrazoles 1−4 contains an azo group which may be regarded as a preformed nitrogen molecule. It is well known that such compounds may extrude molecular nitrogen on irradiation or at higher temperatures[1]. We have studied the gas-phase thermolysis of 1−4 at low pressure (50 Pa) and various temperatures using real-time gas analysis by photoelectron spectroscopy[5]. In all experiments, the onset of thermolysis was indicated by the appearence of the characteristic ionization bands of molecular nitrogen (15.60, 16.98, 18.78 eV[15]). After elimination of molecular nitrogen, reactive species remain which, like the parent trimethylenemethane, may cyclize. As during photolysis[16, 17], this may occur in two directions, affording either 2,2,3,3-tetramethylcyclopropane derivatives (least motion products) or three-membered rings containing the former 4-substituent of the dihydropyrazole (non-least motion products). Diazenylallyl diradicals formed through single-bond cleavage[18] may be intermediates on the path to the trimethylenemethane type diradicals or on the route, by-passing the latter, to the three-membered ring

products. At higher temperatures, the three-membered ring compounds may undergo further reactions.

3,5-Dihydro-3,3,5,5-tetramethyl-4H-pyrazol-4-one (1): The flash vacuum pyrolysis of the dihydropyrazolone 1 at 500°C was reported by Mock to give approximately equal amounts of 2,3-dimethyl-2-butene (6) and the unsaturated ketone 7[19]. Engel and Shen also noted the unexpected reluctance towards photolysis and the thermal stability of 1, 65% of which survived heating to 205°C for 4.5 hours[20]. Subsequently, photolysis and a more detailed study of the thermal cleavage were reported by Quast, Adam et al.[17, 21] who found that, depending on the experimental conditions, several compounds were produced in variable ratios. A flash vacuum pyrolysis at 400°C/730 Pa, similar to the experiments described below, produced 2,4-dimethyl-1-penten-3-one (7) (73%) and 2,3-dimethyl-2-butene (6) (27%) but no acetone azine (8), which was, however, formed as a minor product by photolytic decarbonylation of 1[17, 21].

We have found that the gas-phase thermolysis of the dihydropyrazolone 1 (660°C/10 Pa), which was controlled by PE spectroscopy, affords neither acetone azine (8) nor the unsaturated ketone 7. The PE spectrum of 8 has been measured by Kirste, Poppek, and Rademacher[22]. In addition, we have recorded the PE spectra of pure samples of 6 and 7. By a comparison of these spectra with those of the gas-phase thermolysis of 1, it is evident that 6, molecular nitrogen, and carbon monoxide are produced. The formation of 6 can only be rationalized if 2,2,3,3-tetramethylcyclopropanone (5) is an intermediate. This has also been found in the photolysis of 1, for which the formation of 5 was proven by trapping experiments[17]. There are two additional bands (8.2 and 9.76 eV) in the PE spectrum of 1 (660°C/10 Pa), which do *not* belong to 6, molecular nitrogen, or carbon monoxide, and which we tentatively assign to the cyclopropanone 5. This conclusion is supported by MNDO[11] calculations and comparison with the ionization potentials and ε values of the parent cyclopropanone[23] and *trans*-2,3-di-*tert*-butylcyclopropanone[24]. A PE spectrum of 5 has not been measured until now, because the compound was obtained only in dilute solution[25a].

In summary, the thermolysis of 1 follows the least motion path leading to the cyclopropanone 5, which subsequently loses carbon monoxide. Probably, the missing ketone 7,
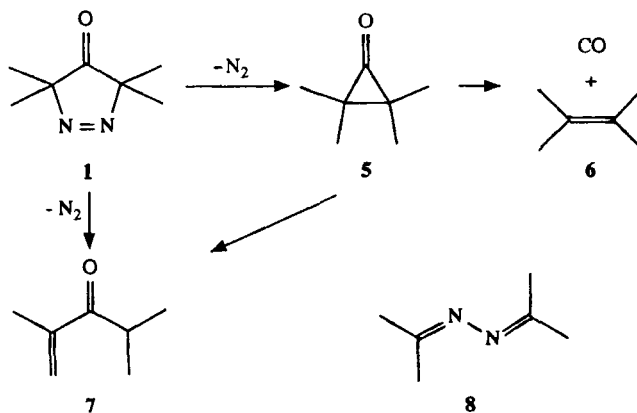
which has previously been observed in the products of thermolysis of 1[19, 21] and also in the attempted gaschromatography of 5[25a], cannot be formed from 1 and/or 5 because the high-vacuum/real-time analysis conditions of the present study favor only unimolecular reactions. The previous occurrence of 7 may well be the result of higher order reactions induced by the particular experimental conditions[19, 21, 25a]. In fact, the analogous cleavages of aziridinones (α-lactams) and aziridinimines affording α,β-unsaturated amides[26] and amidines[27], respectively, have been shown to be base-induced reactions rather than thermolyses.

3,5-Dihydro-3,3,5,5-tetramethyl-4H-pyrazole-4-thione (2): The photolysis and thermolysis of the thione 2 have been investigated by Quast and Fuß[17, 28]. Photo-extrusion of molecular nitrogen from 2 affords the methylenethiirane 9 as the only product. The thermolysis of 2 in benzene solution at 141°C follows a first-order rate law ($k = 2.4 \cdot 10^{-5}$ s^{-1}) and yielded 40% of the methylenethiirane 9. Higher yields

are precluded by the thermal instability of 9 which was already noted by Hortmann and Bhattacharjya[29]. In a reinvestigation, Furuhata and Ando[30] identified the dienethiol 10 as the thermolysis product of 9 and postulated thioallyl diradicals 11 as intermediates. We now studied the gasphase thermolysis of 2 at temperatures between 400 and 880°C. Besides molecular nitrogen, three products were identified, which were formed in different ratios depending on the temperature (Figure 2).

At 880°C/40 Pa, 2 decomposes into unidentified products, and it is not surprising that the signal of hydrogen sulfide at 10.48 eV[15] is observed. The PE spectrum at 640°C shows more characteristic bands in addition to those of molecular nitrogen. By comparison with the PE spectrum of authentic 2,4-dimethyl-1,3-pentadiene-3-thiol (10), all bands in the 640°C PE spectrum have been identified. The dienethiol 10 has been reported as the only product formed in the flash vacuum pyrolysis of 2 (520°C/133 Pa) and 3-isopropylidene-2,2-dimethylthiirane (9) (460°C/133 Pa)[30], and we therefore expected to observe it under our conditions.

It was surprising, therefore, to find at lower temperatures a different PE spectrum which, besides the bands of the starting material 2, contained bands *not* belonging to the dienethiol 10. As the solution thermolysis and photolysis of 2 are known to afford the thiirane 9[17, 28], we investigated the possible occurrence of this compound under our pyrolysis conditions. To this end, 9 was synthesized[28, 29] and its PE spectrum was recorded at different temperatures.

The spectrum of the thiirane 9 at 20°C shows four ionization bands in the region from 7 to 11 eV (Figure 3). A less structured region with some maxima follows at energies above 12 eV. The ionization potentials are given in Table 2. MNDO[11], AM1[12], and PM3[13] calculations also reveal four high-lying occupied molecular orbitals above the various σ levels. PERVAL[31] plots of these MOs are shown in Figure 4. Aue et al.[32] published the PE spectrum of the unsubstituted thiirane and assigned the first band (9.03 eV) to the lone pair of the sulfur atom (n_S) and the next two bands (11.37 and 11.93 eV) to Walsh orbitals of the three-membered ring. In the thiirane 9 there is a C=C bond next to the sulfur atom. The interaction of n_S with the π orbital of the C=C double bond leads to two π-type MOs ($\pi^-_{n_S/C=C}$ and $\pi^+_{n_S/C=C}$). Planckaert, Doucet, and Sandorfy[33] and Bock et al.[34] found that in the similar acyclic compound, methyl vinyl thioether, the two π MOs are separated by 2.55 eV.

We expect the four highest occupied MOs of 9 to be π^+, π^- (a″ symmetry) and two MOs similar to the Walsh orbitals ω_A and ω_S (a′ symmetry). The orbitals in Figure 4 are closely related to these MOs. The assignment of the ionization potentials to the MOs on the basis of the Koopmans approximation[8] is not unequivocal since the energy difference of the second and the third highest occupied MO is rather small (< 0.2 eV) and the various methods of calculation predict different sequences (Table 2). The separation of the second and the third vertical ionization potential in the PE spectrum of 9 is approximately 0.4 eV. The $\pi_{C=C}$ ionization potential of 2-isopropylidene-1,1-dimethylcyclo-
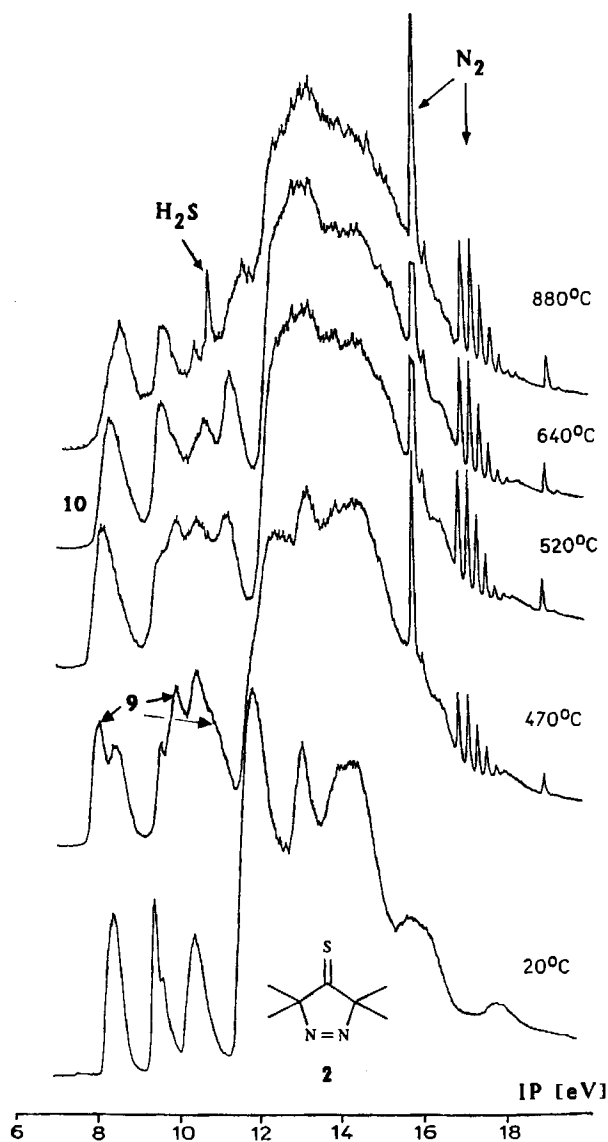

Figure 2. PE spectra of the 3,5-dihydro-4H-pyrazole-4-thione 2 recorded at 20, 470, 580, 640, and 880°C indicating the products 9, 10, hydrogen sulfide, and molecular nitrogen

propane (11), which has a similar $C=C$ bond, is found at 8.46 eV (Table 3), i.e. 0.59 eV above $\pi^-_{n_S/C=C}$ of 9. If we assume a symmetrical orbital interaction between n_S and $\pi_{C=C}$ in 9, we expect $\pi^+_{n_S/C=C}$ ca. 0.59 eV below n_S of thiirane, i.e. at $-9.03 - 0.59 = -9.62$ eV. Therefore, the second ionization potential of 9 (9.84 eV) rather than the third (10.21 eV) is assigned to this MO. The third and the fourth ionization potentials are then assigned to ω_A and ω_S, respectively.

We have also recorded the PE spectrum of 9 at higher temperatures and have obtained the same spectra as in the pyrolysis of the thione 2 but without the bands of molecular nitrogen. Furthermore, the bands of 9 are not superimposed to those of 2 as in the thermolysis of 2 at temperatures below 500°C. The PE spectrum of the thiirane 9 is observed at temperatures as high as 410°C. At temperatures above 550°C, the spectrum of the dienethiol 10 is prevailing, above
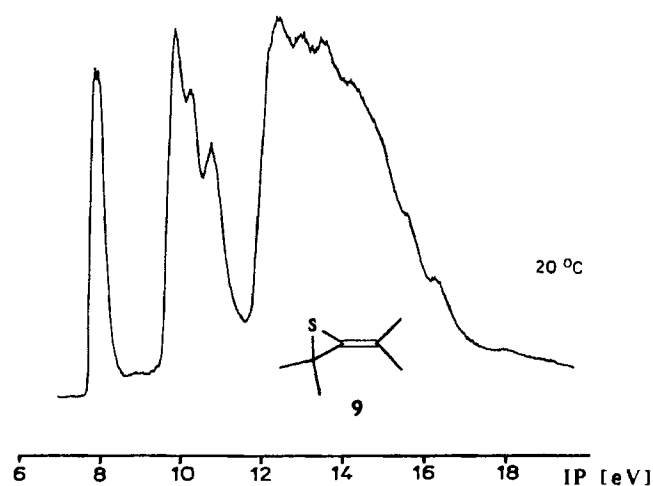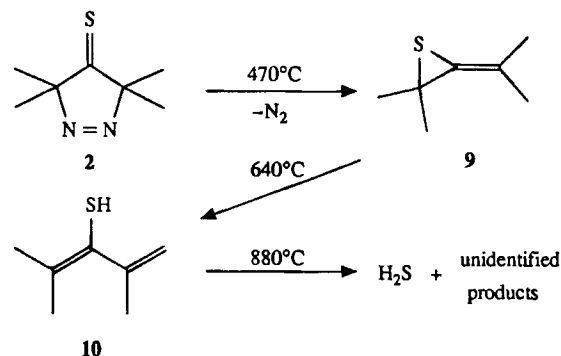
800°C, further decomposition is indicated by the appearance of a hydrogen sulfide band at 10.84 eV.

The PE spectrum recorded during the pyrolysis of 2 at 470°C provides unequivocal evidence for the occurrence of the methylenethiirane 9 by the signals at 7.87 and 9.84 eV. A further signal of 9 is seen as a shoulder at 10.7 eV. Bands at 8.3, 9.4, and 10.3 eV stem from intact thione 2. The PE spectrum recorded at 520°C seems to be a combination with that of the dienethiol 10.

Table 2. Vertical ionization potentials I_v [eV] and calculated orbital energies ε [eV] of the methylenethiirane 9

Band	I_v	Assignment	$-\varepsilon$ (MNDO)	$-\varepsilon$ (AM1)	$-\varepsilon$ (PM3)
1	7.87[a]	$\pi^-_{n_S/C=C}$	9.38	9.00	8.68
2	9.84	$\pi^+_{n_S/C=C}$	11.20	10.92	11.00
3	10.21	ω_S	11.38	10.84	10.90
4	10.74	ω_A	12.00	11.58	11.93
5	12.36				
6	12.94				
7	13.43				
8	14.20				

[a] Vibrational splitting: 640 cm^{-1}.

Figure 3. PE spectrum of 3-isopropylidene-2,2-dimethylthiirane (9)
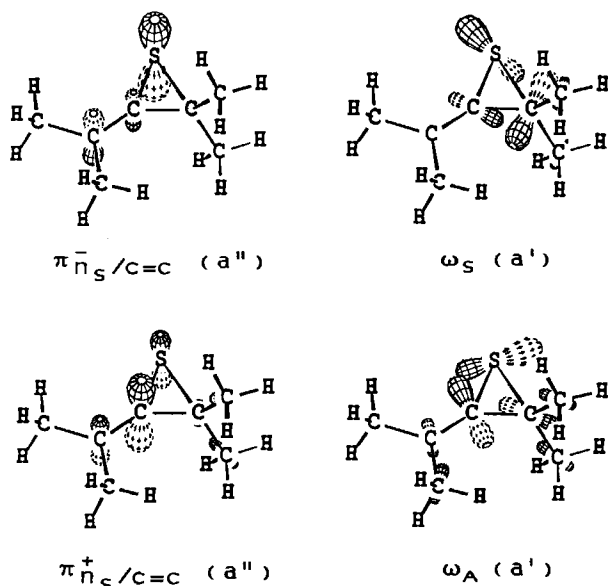
Figure 4. The four highest occupied molecular orbitals of thiirane 9

The detection of the methylenethiirane 9 in the PE-controlled gas-phase pyrolysis of 2 is at variance with the results of flash vacuum pyrolysis of 2 carried out at virtually the same temperature which afforded only the dienethiol 10. The latter result gave rise to speculations about the intervention of planar, C_{2v}-symmetrical thioxyallyl diradicals in the $^1A_1$ and $^1B_1$ state ($^1A_1$-12, $^1B_1$-12)[30] (Scheme 1).

Scheme 1
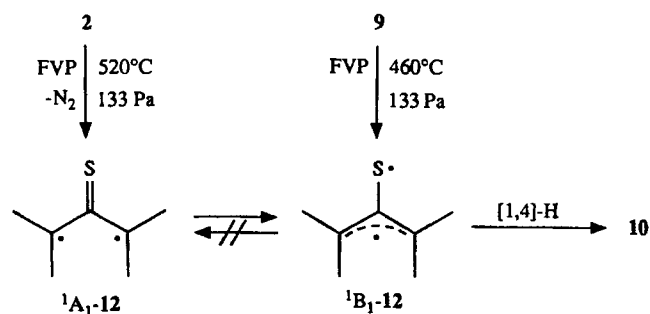
Under the conditions of the present study, the methylenethiirane 9 is the primary observable product of the thermal extrusion of molecular nitrogen from the thione 2. The variable temperature PE spectra of pure 9 show that 9 has a life-time sufficient for PE detection at temperatures which induce thermal cleavage of 2. At higher temperatures, the former can rearrange to the dienethiol 10 either via thioxyallyl diradicals (e.g. 12) or by a concerted 1,5-hydrogen shift. The mechanism of this isomerization may be related to the course of the thermal ring-opening of tetramethylcyclopropanone (5) affording the unsaturated ketone 7. At more drastic conditions (880°C), the dienethiol 10 decomposes to hydrogen sulfide and other not identified products.

Thus, the detection of the methylenethiirane 9 under both sets of experimental conditions, i.e. solution thermolysis[28] and gas-phase pyrolysis of the thione 2, allows a rationalisation of the formation of the dienethiol 10 in terms of a reaction sequence involving 9 as a crucial intermediate.

3,5-Dihydro-3,3,5,5-tetramethyl-4-methylene-4H-pyrazole (3): Following Crawford's pioneering search for trimethylenemethane in the pyrolysis of 3,5-dihydro-4-methylene-4H-pyrazole[35], the thermolyses of numerous 4-alkylidene-3,5-dihydro-4H-pyrazoles have been investigated and have opened a Pandora's box of results[1,18,36,37]. The thermal extrusion of molecular nitrogen from such compounds has also been the subject of theoretical studies[38]. In particular, gas-phase thermolysis of the 3,5-dihydro-4-methylene-4H-pyrazole 3 at temperatures between 165 and 200°C has the activation parameters $\Delta H^{+} = 166.5 \pm 1.7$ kJ mol^{-1}, $\Delta S^{+}_{150°C} = 41 \pm 4$ J K^{-1} mol^{-1} and affords a rapidly equilibrating ($\Delta H^{+} = 149.0 \pm 0.1$ kJ mol^{-1}, $\Delta S^{+}_{150°C} = 17 \pm 4$ J K^{-1} mol^{-1}) mixture of the methylenecyclopropanes 11 and 13, which contains only 0.16—0.35% of the latter at 180—259°C ($\Delta H = -21.7 \pm 0.6$ kJ mol^{-1}, $\Delta S_{150°C} = 6.0 \pm 0.9$ J K^{-1} mol^{-1} for the conversion of 13 to 11)[36].

For the thermolysis of 3 at much higher temperatures, PE spectra are observed which do not vary over a wide range (500—720°C/50 Pa). At lower temperatures there are bands from the starting material; at higher temperatures no characteristic bands are seen because of total decomposition. Therefore, we measured the PE spectra of pure samples of 11 and 13 (Table 3).

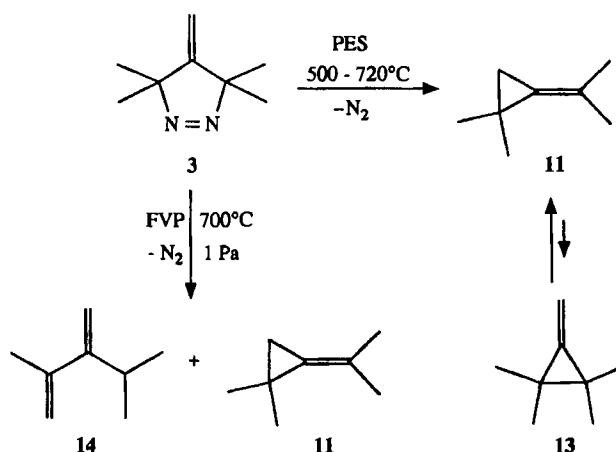A comparison with the PE spectra from thermolysis at 500—720°C shows that 11 is the only product besides molecular nitrogen. No 13 has been observed, and there are no unassigned bands. The isopropylidenecyclopropane 11 is stable under these conditions, and an acyclic compound, e.g. 14, as in the thermolysis of 2, could not be found, although dienes of type 14 have been observed in other cases[37]. If we assume thermodynamic product control, which seems reasonable in view of the high temperature, then the exclusive observation of the non least motion product 11 is readily explained in terms of the low equilibrium concentrations of its isomer 13[36], which are below the limit of detection by PE spectroscopy.

3,5-Dihydro-3,3,5,5-tetramethyl-4-(methylimino)-4H-pyrazole (4): At temperatures just above 600°C (40 Pa), the thermolysis of 4 is complete, and the signals of the starting

Table 3. Vertical ionization potentials I_v [eV] and calculated orbital energies ε [eV] of the methylenecyclopropane derivatives 11 and 13

Band	I_v	Assignment	− ε (MNDO)	− ε (AM1)	− ε (PM3)
2-Isopropylidene-1,1-dimethylcyclopropane (11)					
1	8.46[a]	π_{CC}	9.76	9.39	9.49
2	9.53	ω_S	10.87	10.43	10.78
3	10.20	ω_A	11.25	10.97	11.38
4	11.84	π_{CMe_2}	12.59	12.02	12.46
5	12.00				
6	12.92				
7	13.32				
8	15.34				
9	16.1				
1,1,2,2-Tetramethyl-3-methylenecyclopropane (13)					
1	9.22	π_{CC}	10.10	10.16	10.28
2	9.44	ω_S	10.72	10.27	10.62
3	9.92	ω_A	10.87	10.28	10.63
4	11.28	π_{CMe_2}	12.24	11.60	11.70
5	12.6				
6	13.43				
7	14.87				
8	15.7				
9	16.6				

[a] Vibrational splitting: 1450 cm^{-1}.

imine 4 have disappeared (Figure 5). Besides the bands of molecular nitrogen, the PE spectra show a sharp peak at 11.28 eV arising from methyl isocyanide (15)[39] as well as bands of 2,3-dimethyl-2-butene (6). As 6 and 15 are the expected thermolysis products of 2,2,3,3-tetramethylcyclopropanimine (16)[17,28], it is safe to postulate the latter as the cyclization product of intermediate diradicals evolving from 4, although bands which could be attributed to 16 are missing. Thus, the gas-phase thermolysis of the imine 4 at temperatures above 600°C proceeds in the same way as photolysis[17] and as pyrolysis of the corresponding dihydropyrazolone 1.

Flash Vacuum Pyrolyses of the 3,5-Dihydro-4H-pyrazoles 1—3

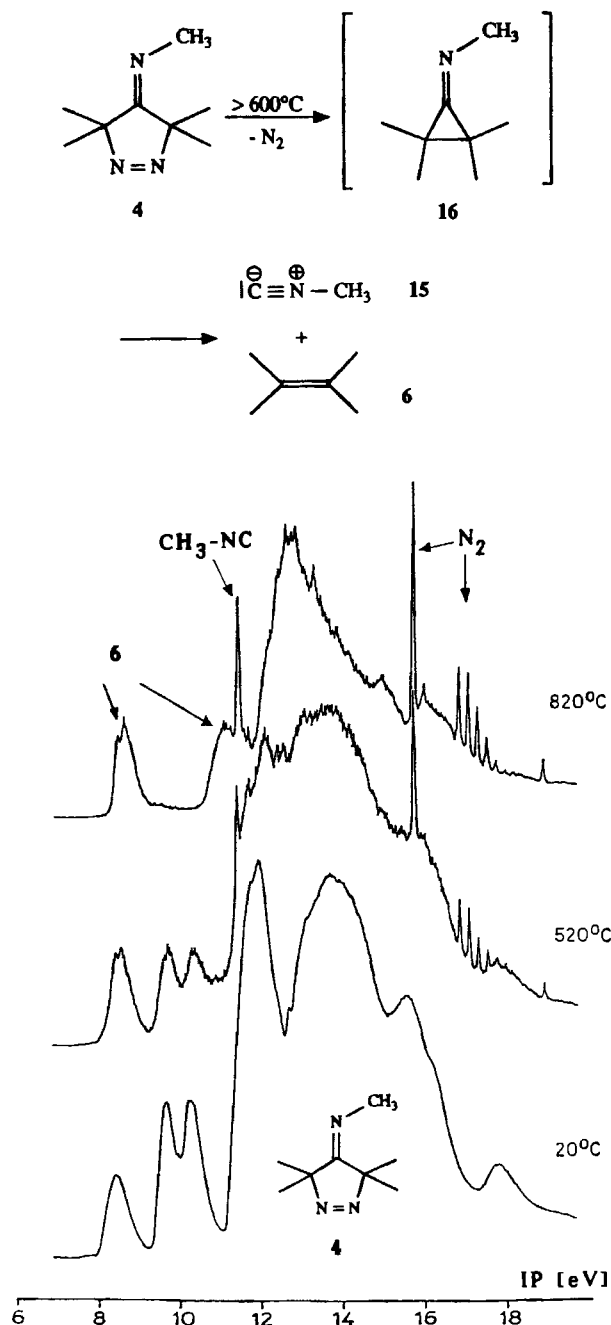In addition to the investigations by PE spectroscopy, we used flash vacuum pyrolysis[6] to study the thermal decom-

Figure 5. PE spectra of the 3,5-dihydro-4-(methylimino)-4H-pyrazole 4 recorded at 20, 520, and 820°C indicating the products 2,3-dimethyl-2-butene (6) and methyl isocyanide (15)

position of some 3,5-dihydro-4H-pyrazoles in order to clarify the differences and similarities in the behavior of these compounds. The methylene compound 3 was pyrolysed at 650 and 700°C, and at both temperatures two products were found in variable ratios. At the lower temperature, the isopropylidenecyclopropane 11 was identified as the dominant product. The minor product, which at 700°C was obtained in the same yield as 11, was identified as 2,4-dimethyl-3-methylene-1-pentene (14) by NMR and mass spectroscopy, but was not isolated. Until now, only its synthesis[40] but no spectroscopic data have been published.

Flash vacuum pyrolysis of the pyrazolinethione 2 produced only the acyclic dienethiol 10, which was also obtained in the PE-controlled thermolysis at higher temperatures. In order to further substantiate the difference in the behaviour of ketone 1 and thioketone 2, we pyrolysed both together, so that the same conditions were guaranteed (550°C/0.5 Pa). The reaction of the thioketone 2 gave the unsaturated thiol 10 as the only product, whereas 1 formed equal amounts of the alkene 6 and the acyclic unsaturated ketone 7.

Curie-Point Pyrolysis of 3,5-Dihydro-3,3,5,5-tetramethyl-4H-pyrazol-4-one (1)

For a comparison with the results of the vacuum pyrolyses described above, we also studied the pyrolysis of the ketone 1 in a stream of helium at higher pressure (ca. 10^5 Pa) using a Curie-point pyrolyser attached directly to a gas chromatograph which was linked to a mass spectrometer[41]. Due to the volatility of the ketone 1, little decomposition was observed at temperatures below 1000°C and slow heating rates. At a Curie point of 1000°C and a heating rate of 75°C/ms, approximately half of the ketone 1 decomposed affording five products in addition to 2,3-dimethyl-2-butene (6) and the enone 7 observed previously[21]. Comparison of the mass spectra of the pyrolysis products with reported spectra[42] or spectra of authentic samples (6, 7) allowed the identification of propene, 2-methyl-2-butene, 6, 2,3-dimethyl-1,3-butadiene, and enone 7 (in the order of increasing retention times). The ratio of the major products (80%), 6 and 7, varied between 52:48 and 70:30, while each of the other alkenes formed 5 ± 3% of the products. Two minor fragments were not identified. Acetone azine (8) was not observed.

2-Methyl-2-butene and 2,3-dimethyl-1,3-butadiene are probably derived from 6. Thus, except for propene, the products of the Curie-point pyrolysis closely resemble those of the flash vacuum pyrolysis. The formation of small amounts of propene, however, may be indicative of a further decomposition route affording as primary products 2-diazopropane and dimethylketene in a [3+2]cycloreversion of ketone 1.

Conclusion

The thermolyses of 3,5-dihydro-4H-pyrazoles 1−4 give rise to several products. Temperature is the most important factor for the product distribution, but there are also differences between pyrolysis in the PE spectrometer and flash vacuum pyrolysis. The results are summarized in Table 4.

The results show that under the conditions of flash vacuum pyrolysis mainly the more stable acyclic products (6, 7, 10, 14) are formed. The dienethiol 10 is also produced at higher temperatures in the PE-controlled pyrolysis. The two methods are complementary. Whereas it is sometimes easier to obtain the stable products of thermolytic processes from flash vacuum pyrolysis, the reactions in the PE spectrometer permit the study of short-lived intermediates, which would decompose and/or rearrange under the former conditions. The experimental conditions of the PE-controlled real-time

Table 4. Products of gas-phase thermolyses of the 3,5-dihydro-4H-pyrazoles 1 – 4 studied by photoelectron spectroscopy (PES) and flash vacuum pyrolysis (FVP)

Compd.	X	Method	Tempera-ture [°C]	Products[a]
1	O	PES	660	6, CO
		FVP	550	(6 + CO)/7 = 1:1
2	S	PES	470	9
			640	10
			880	H_2S and unidentified products
		FVP	550	10
3	CH_2	PES	500 – 720	11
		FVP	700	11, 14
4	NCH_3	PES	600	6, 15

[a] Besides molecular nitrogen.

gas analysis allow the detection of products with life times greater than ca. 0.1 s. Furthermore, the PE study in the gas-phase excludes solvent effects, and no information is lost due to subsequent reactions during workup and analysis of the products.

The PE spectra indicate that, in the gas-phase thermolyses of the 3,5-dihydro-4H-pyrazoles 1 – 4, three-membered rings are formed as primary products together with molecular nitrogen. In a second step, the three-membered rings may isomerize to acyclic compounds or decompose in a [2 + 1] cheletropic reaction to molecules such as the alkene 6 and carbon monoxide or methyl isocyanide (15).

Experimental

PE Spectra: UPG 200 spectrometer of Leybold-Heraeus equipped with a He(I) lamp (21.21 eV) as radiation source. The spectra were calibrated with the lines of xenon at 12.130 and 13.436 eV and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for the ionization potentials, for broad or overlapping signals it was only ±0.05 eV.

Thermolyses were carried out at 10 – 50 Pa in a molybdenum tube of 80 mm length and 4.5 mm inner diameter, which was placed between the sample inlet system and the ionization chamber. The distance between thermolysis tube and ionization chamber was about 35 mm. Temperatures are accurate to ca. ±5°C.

Flash Vacuum Pyrolyses were carried out in an apparatus according to Seybold and Jersak[43]. The quartz tube had a length of 350 mm and an inner diameter of 22 mm. The products were condensed on a cold finger (−196°C). About 2 – 3 g of 1 – 3 were pyrolysed at pressures of 1 Pa or lower.

Curie-Point Pyrolysis: Varian model 9250 Pyroprobe pyrolyser directly attached to a gas chromatograph Varian 2700, which was linked by a Watson-Biemann-type diffusion separator to a CH-7 mass spectrometer equipped with the data system SS 200, both of Varian-MAT. A 3 m x 1/8″ stainless steel column packed with 10% Carbowax 4000 on Volaspher A_2 (Merck) was used. Carrier gas: helium; temperature program 20 – 150°C at 6°C min⁻¹. The chromatograms were monitored either by means of the flame ionization

detector of the gas chromatograph or by recording the total ion current in the mass spectrometer, which was operated at 70 eV. The mass spectrum for each peak was scanned near or at the peak maximum. Sample size approximately 1 mg, pyrolysis temperature 1000°C, held for 20 s, heating rate 75°C/ms.

Syntheses of the pyrazolines 1[19, 28, 36], 2[17, 28, 44], 3[36, 44], and 4[16, 28] have been described in the literature. Also compounds 7[45], 9[28−30], and acetone azine (8)[22] were synthesized according to literature procedures. 2,3-Dimethyl-2-butene (6) is commercially available. The dienethiol 10 and the methylenecyclopropane 11 were synthesized by preparative flash vacuum pyrolysis from 2 and 3, respectively, as described above; pure samples were obtained by trap-to-trap distillation and characterized by literature data[30, 46]. The methylenecyclopropane 13 was a gift by Professor *P. Binger*, Max-Planck-Institut für Kohlenforschung, Mülheim a. d. Ruhr. – The diene 14 was identified by the following spectroscopic data: ¹H NMR (200 MHz, CDCl₃): δ = 1.01 [d, J = 7 Hz, 6H, CH(CH₃)₂], 1.84 [s, 3H, =C(CH₃)−], 2.62 [sept, J = 7 Hz, 1H, CH(CH₃)₂], 4.88 (unresolved multiplet, 2H, CH₂), 5.00 (s, 2H, CH₂). – ¹³C NMR (50.3 MHz, CDCl₃): δ = 155.1 (quat. C), 143.1 (quat. C), 118.6 (CH₂), 108.6 (CH₂), 29.5 (CH), 22.6 (CH₃), 21.8 (CH₃). – MS (70 eV): m/z (%) = 110 (32) [M⁺], 95 (50) [M⁺ − CH₃], 81 (9) [M⁺ − C₂H₅], 67 (90) [M⁺ − C₃H₇], 55 (72) [M⁺ − C₄H₇], 41 (100) [C₃H₅⁺].

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