

Flash Vacuum Pyrolysis and Photolysis of 3,3,5,5-Tetramethylpyrazolin-4-one – A Matrix Isolation Study

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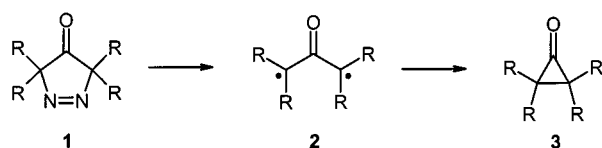
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The flash vacuum pyrolysis of 3,3,5,5-tetramethylpyrazolin-4-one (**4**) with subsequent trapping of the products in argon at 10 K results in the formation of a complex product mixture with tetramethylcyclopropanone (**5**) as one of the minor constituents. The 193 nm photochemistry of matrix-isolated **4** is much cleaner, yielding cyclopropanone **5** and allene

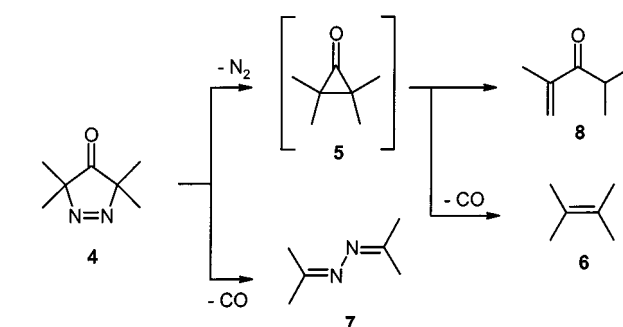
oxide **9** as the major products. The reaction of tetramethylallene **13** with oxygen atoms yields the same product mixture of **5** and **9** and thus provides an independent route to these species. The experimental IR spectra of **5** and **9** are in good agreement with the results from DFT calculations.

Introduction

The elimination of nitrogen from pyrazolinones **1** leads to highly reactive species such as oxyallyl diradicals **2** and cyclopropanones **3**. The photochemistry and thermolysis of 3,3,5,5-tetramethylpyrazolinone **4** in solution was investigated by Quast and co-workers.^[1]



The main product of irradiation at $\lambda > 300$ nm of **4** was 2,3-dimethyl-2-butene **6** (up to 80%), presumably formed by loss of CO from tetramethylcyclopropanone (**5**). The cyclopropanone **5** was not directly observed, but could be trapped with methanol.^[1a] A second product of the photolysis was acetone azine **7**, produced by elimination of CO from **4** (Scheme 1). Short-wavelength (185 nm) UV irradiation yields 2,4-dimethylpent-1-en-3-one (**8**) as the main product along with alkene **6** and azine **7** as minor constituents.^[1b] This was rationalized by the assumption that cyclopropanone **5** was the main product at both 300 nm and 185 nm irradiation. Secondary photolysis of **5** results in decarbonylation to **6** or in rearrangement to ketone **8**.



Scheme 1

The flash vacuum pyrolysis (FVP) of pyrazolinone **4** was investigated under a variety of conditions and product identification carried out by gas chromatography or photoelectron spectroscopy.^{[1b][2]} The major products were again enone **8** and alkene **6**, while ketazine **7** was not formed during the pyrolyses. This suggests that in the thermal reaction the elimination of nitrogen is more efficient than during the photolyses.

Matrix isolation spectroscopy is ideally suited to identify labile reaction intermediates, which can be produced by FVP with subsequent trapping in low-temperature matrices or by direct irradiation of matrix-isolated precursors. Here we describe a detailed mechanistic study of the photolysis and pyrolysis of pyrazolinone **4** using the matrix isolation technique.^[3]

Results

Matrix Photolysis of Pyrazolinone **4**

The IR spectrum of pyrazolinone **4**, matrix-isolated in argon at 10 K, exhibits a very strong absorption at 1771

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cm^{-1} ($\text{C}=\text{O}$ stretching vibration) and a strong absorption at 1524 cm^{-1} ($\text{N}=\text{N}$ stretching vibration). In agreement with literature data, pyrazolinone **4** is photochemically stable to irradiation at $\lambda > 350\text{ nm}$.^[4] However, 60 min irradiation at $\lambda = 248\text{ nm}$ (KrF Excimer Laser) results in a decrease of **4** and formation of small amounts of 2,3-dimethyl-2-butene (**6**), tetramethylcyclopropanone (**5**), and CO, all readily identified by comparison of the IR spectra with literature data.^{[5][6]}

Irradiation of **4** at $\lambda = 193\text{ nm}$ (120 pulses, 60 mJ/pulse, ArF Excimer Laser) produces high yields of cyclopropanone **5** and allene oxide **9**, but only traces of ketazine **7** (1655 and 1365 cm^{-1} , Figure 1). Cyclopropanone **5** was identified by its characteristic band at 1844 cm^{-1} (carbonyl absorption) and absorptions at 1823 and 967 cm^{-1} which are in a good agreement with the IR data reported by Haller and co-workers^[5] and Sorensen and co-workers.^[6] (the absorption at 1823 cm^{-1} is a Fermi resonance of the vibrations at 967 and 1844 cm^{-1}). A DFT calculation at the B3LYP/6-311G++(d,p) level of theory leads to an excellent reproduction of the experimental spectrum (Table 1).

The second major product is the allene oxide **9**, which was identified by comparison of the experimental IR spectra with data calculated at the B3LYP/6-311G++(d,p) level

of theory (Figure 1, Table 2). The most intense absorption in the IR spectrum of **9** is the $\text{C}-\text{O}$ stretching mode at 1147 cm^{-1} (B3LYP: 1140 cm^{-1}). Since the $\text{C}=\text{C}$ stretching vibration of **9** is located in the same area as the strong absorption of **5** at 1823 cm^{-1} , this vibration is not observed in our experiments (Figure 1, Table 2). Otherwise, the experimental and calculated IR data are in good agreement. In the parent methylenoxirane the $\text{C}=\text{C}$ stretching vibration is found at 1824 cm^{-1} and the $\text{C}-\text{O}$ stretching vibration at 1109 cm^{-1} .^[7-9]

Further irradiation (420 pulses) leads to rearrangement of **9** to **5** and its subsequent decarbonylation affording **6** (1452 , 1369 and 1170 cm^{-1} , identified by comparison with an authentic matrix-isolated sample). After 1200 pulses, propene (**10**) (908 and 1448 cm^{-1}) is formed as a further fragmentation product (Scheme 2).

Quantum chemical calculations predict that **5** is slightly more stable than **9** [B3LYP/6-311++G(d,p) + ZPE: 0.42 kcal/mol , MP2/6-31G(d): 2.80 kcal/mol]. Oxirane **9** is only observed after the first pulses at $\lambda = 193\text{ nm}$, prolonged irradiation leads to cyclopropanone **5** and its decomposition products. The related rearrangement of di-*tert*-butylallene oxide to di-*tert*-cyclopropanone has been reported by Chan and co-workers.^[10]

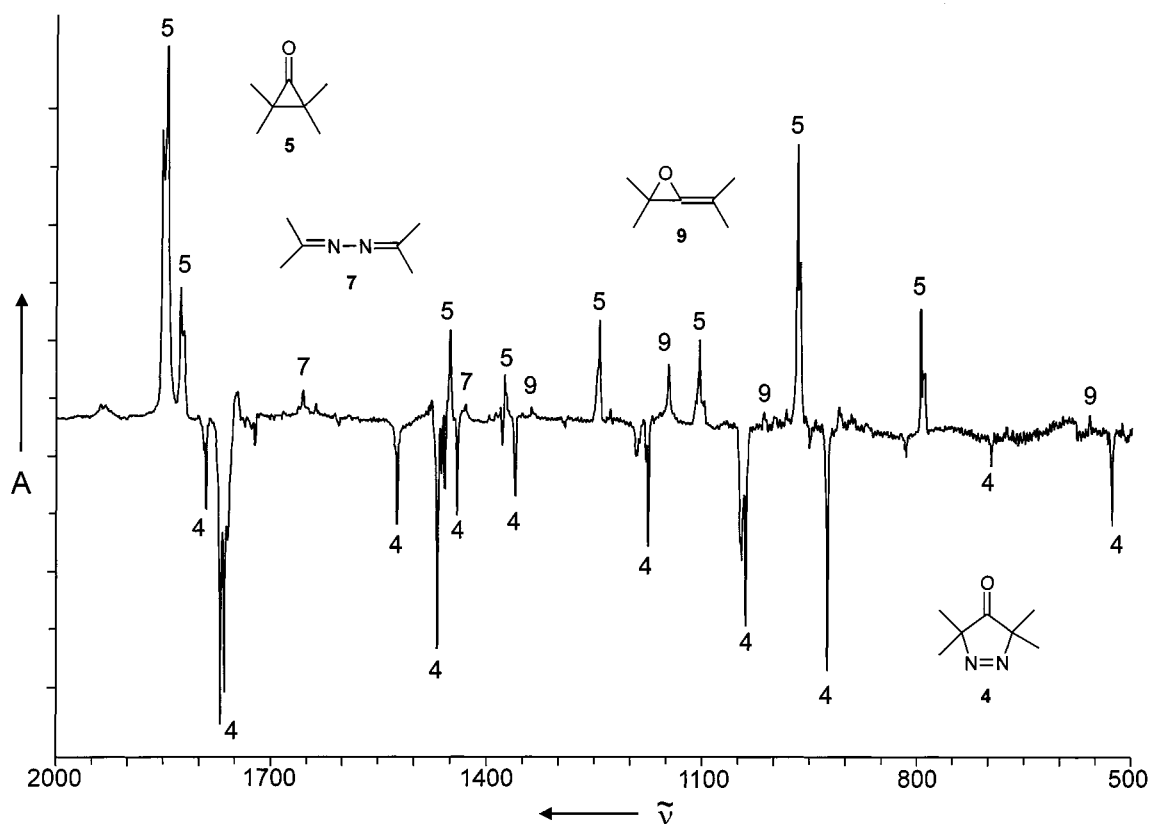
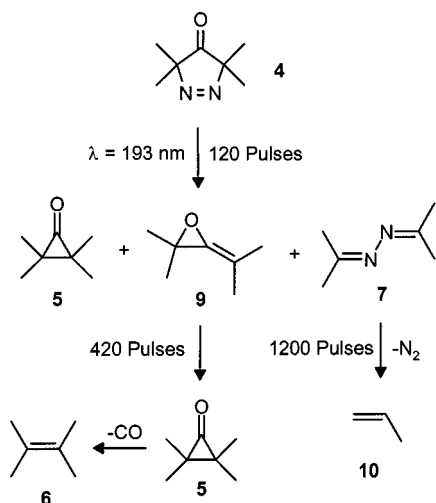


Figure 1. IR difference spectrum showing the photolysis of **4** in argon at 10 K after irradiation of a matrix of **4** with $\lambda = 193\text{ nm}$; bottom part: bands of **4** disappearing; top part: bands of **5** and **9** appearing on irradiation.

Table 1. Comparison of IR spectroscopic data of tetramethylcyclopropanone **5**, matrix-isolated in argon at 10 K, with calculations at the B3LYP/6-311++G(d, p) (scaled by 0.97) and at the MP2/6-31G(d) (scaled by 0.95) level of theory

Nr. ^[a]	Sym	5 (¹⁶ O) argon, 10 K $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	5 (¹⁸ O) argon, 10 K $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	[ν_i/ν_j]	5 (¹⁶ O) B3LYP/ 6-311++G (d, p) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	5 (¹⁸ O) B3LYP/ 6-311++G (d, p) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	[ν_i/ν_j]	5 (¹⁶ O) MP2/ 6-31G(d) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	5 (¹⁸ O) MP2/ 6-31G(d) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	[ν_i/ν_j]	Assignment ^[c]
13	b ₂	—	—	—	—	—	—	573 (1)	571 (1)	0.996	
14	a ₁	—	—	—	—	—	—	612 (1)	612 (1)	1.000	
17	b ₂	794 (24)	794 (37)	1.000	773 (6)	771 (6)	0.998	780 (12)	778 (12)	0.998	
19	b ₂	967 (62)	967 (33)	1.000	942 (21)	942 (22)	1.000	958 (41)	958 (42)	1.000	C—C def.
20	b ₁	—	—	—	—	—	—	959 (1)	959 (1)	1.000	
21	a ₁	—	—	—	—	—	—	986 (1)	984 (1)	0.998	
24	b ₂	1105 (8)	—	—	1095 (4)	1095 (4)	1.000	1113 (5)	1113 (5)	1.000	C—C str.
25	a ₁	—	—	—	—	—	—	1123 (1)	1123 (1)	1.000	C—C str.
28	b ₂	1245 (16)	1244 (12)	0.999	1223 (6)	1223 (6)	1.000	1252 (15)	1252 (15)	1.000	combination
31	b ₁	1384 (4)	—	—	1366 (1)	1366 (1)	1.000	1386 (3)	1386 (3)	1.000	
32	b ₂	—	—	—	—	—	—	1391 (1)	1391 (1)	1.000	
36	b ₁	—	—	—	—	—	—	1472 (1)	1472 (1)	1.000	
37	b ₂	1457 (11)	—	—	1447 (4)	1447 (4)	1.000	1475 (8)	1475 (8)	1.000	C—H def.
39	b ₁	1461 (9)	1461 (15)	1.000	1456 (3)	1456 (4)	1.000	1486 (7)	1486 (8)	1.000	
40	a ₁	—	—	—	—	—	—	1491 (1)	1491 (1)	1.000	
41	a ₁	1477 (7)	1477 (8)	1.000	1472 (2)	1472 (2)	1.000	1501 (6)	1500 (6)	1.000	
		1823 (53)	1829 (30)	1.004	—	—	—	—	—	—	Fermi-Resonance
											C=O str.
42	a ₁	1844 (100)	1808 (100)	0.980	1836 (100)	1805 (100)	0.983	1801 (100)	1774 (100)	0.985	
44	b ₂	—	—	—	2926 (16)	2926 (16)	1.000	2939 (21)	2939 (21)	1.000	
45	b ₁	—	—	—	2928 (9)	2928 (10)	1.000	2942 (25)	2942 (15)	1.000	
46	a ₁	—	—	—	2933 (11)	2933 (11)	1.000	2945 (22)	2945 (12)	1.000	
49	b ₁	—	—	—	2982 (9)	2982 (9)	1.000	3017 (10)	3017 (10)	1.000	C—H str.
50	a ₁	—	—	—	2984 (14)	2984 (14)	1.000	3019 (20)	3019 (21)	1.000	
52	b ₂	—	—	—	3013 (8)	3013 (8)	1.000	3042 (14)	3042 (14)	1.000	
53	b ₁	—	—	—	3029 (11)	3029 (11)	1.000	3057 (15)	3057 (15)	1.000	
54	a ₁	—	—	—	3029 (3)	3029 (3)	1.000	3057 (5)	3057 (5)	1.000	

[a] Mode-number from the ab initio calculation. IR bands with relative intensities lower than 0.5 are not tabulated. — [b] Relative intensity based on the strongest absorption (100%). — [c] The assignment is based on the comparison of the calculated and experimental spectrum and is only tentative.

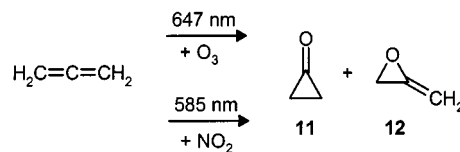


Scheme 2

Oxidation of Tetramethylallene (13) with Oxygen Atoms

The transfer of oxygen atoms to allene in cryogenic matrices was investigated by Singmaster and Pimentel^{[7][8]} and by Nakata and Frei^[9] with ozone and N₂O, respectively, as photolytical sources of the oxygen atoms. In both cases,

cyclopropanone (**11**) and methylenecyclopropane (**12**) were formed and in addition CO, formaldehyde, acrolein, and ketene were produced in the ozone oxidation (Scheme 3). This suggested to us that oxygen transfer to tetramethylallene (**13**) should provide an alternative source of **5** and **9**. In addition, the advantageous use of ¹⁸O₃ as the source of the oxygen atoms should readily lead to incorporation of an ¹⁸O isotopic label into **5** and **9**.



Scheme 3

Irradiation of ozone at $\lambda = 420$ nm rapidly produces O(³P) and O₂, while **13** is completely stable under these conditions. If an argon matrix, doped with **13** and an excess (0.7% in argon) of O₃, is irradiated with 420 nm light, both **13** and O₃ disappear within several minutes, and a complex mixture of oxidation products is formed (Figure 2). Most of the products were identified by comparison of their IR spectra with those of authentic matrix-isolated compounds – if available – or with spectra calculated at the B3LYP/6-311++G(d,p) level of theory. In addition, the oxidation

Table 2. Comparison of IR spectroscopic data of tetramethylallenoxide **9**, matrix-isolated in argon at 10 K, with calculations at the B3LYP/6-311++G(d, p) (scaled by 0.97) and at the MP2/6-31G(d) (scaled by 0.95) level of theory

Nr. ^[a]	Sym	9 (¹⁶ O) argon, 10 K $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	9 (¹⁸ O) argon, 10 K $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	[ν_i/ν_i]	9 (¹⁶ O) B3LYP/ 6-311++G (d, p) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	9 (¹⁸ O) B3LYP/ 6-311++G (d, p) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	[ν_i/ν_i]	9 (¹⁶ O) MP2/ 6-31G(d) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	9 (¹⁸ O) MP2/ 6-31G(d) $\tilde{\nu}$, [cm ⁻¹] (I _{rel}) ^[b]	[ν_i/ν_i]	Assignment ^[c]
12	A''	—	—	—	418 (7)	409 (8)	0.978	412 (10)	402 (11)	0.976	
13	A'	558 (15)	551 (13)	0.987	549 (8)	542 (12)	0.987	537 (12)	529 (16)	0.985	
15	A'	595 (5)	585 (4)	0.983	586 (22)	577 (21)	0.984	590 (20)	583 (19)	0.988	
16	A'	677 (28)	669 (34)	0.988	665 (15)	657 (14)	0.988	667 (17)	659 (16)	0.988	C—C def.
17	A'	872 (20)	870 (18)	0.998	849 (10)	847 (10)	0.998	866 (7)	864 (7)	0.998	
19	A'	957 (14)	954 (16)	0.997	940 (5)	939 (9)	0.999	954 (6)	952 (11)	0.997	
20	A'	981 (13)	—	—	964 (8)	964 (10)	1.000	979 (7)	978 (4)	0.999	
22	A'	1011 (30)	999 (28)	0.988	993 (25)	979 (27)	0.986	1000 (27)	985 (31)	0.985	ring- def.
25	A'	1075 (13)	—	—	1089 (28)	1089 (29)	1.000	1107 (46)	1107 (51)	1.000	combination
26	A'	1147 (100)	1141 (100)	0.995	1140 (100)	1132 (100)	0.993	1156 (100)	1148 (100)	0.993	combination
27	A''	1227 (26)	1227 (23)	1.000	1200 (14)	1200 (15)	1.000	1229 (14)	1229 (15)	1.000	C—C str.
29	A'	1333 (17)	1332 (16)	0.999	1314 (11)	1314 (12)	1.000	1337 (11)	1336 (13)	1.000	C—C str.
30	A''	1376 (80)	1376 (78)	1.000	1363 (3)	1363 (4)	1.000	1385 (23)	1385 (26)	1.000	
31	A'	—	—	—	1364 (16)	1364 (18)	1.000	1388 (6)	1388 (7)	1.000	
32	A'	1396 (vw)	1396 (vw)	1.000	1374 (1)	1374 (1)	1.000	1394 (2)	1394 (2)	1.000	
33	A'	—	—	—	1378 (2)	1378 (2)	1.000	1401 (2)	1401 (2)	1.000	
36	A''	—	—	—	1436 (2)	1436 (2)	1.000	1466 (3)	1466 (3)	1.000	C—H def.
37	A''	1447 (12)	—	—	1443 (4)	1443 (5)	1.000	1472 (16)	1472 (18)	1.000	
38	A'	—	—	—	1445 (13)	1445 (14)	1.000	1475 (6)	1475 (7)	1.000	
39	A'	—	—	—	1448 (2)	1448 (2)	1.000	1477 (3)	1477 (3)	1.000	
40	A'	1451 (15)	1451 (15)	1.000	1454 (10)	1454 (11)	1.000	1480 (15)	1480 (16)	1.000	
42	A'	—	—	—	1827 (48)	1826 (51)	0.999	1829 (42)	1828 (45)	0.999	C=C str.
43	A'	—	—	—	2909 (26)	2909 (28)	1.000	2928 (32)	2928 (36)	1.000	
44	A'	—	—	—	2913 (68)	2913 (75)	1.000	2931 (48)	2931 (54)	1.000	
45	A''	—	—	—	2933 (8)	2933 (8)	1.000	2946 (8)	2946 (9)	1.000	
46	A'	—	—	—	2938 (27)	2938 (30)	1.000	2949 (23)	2949 (26)	1.000	
47	A''	—	—	—	2947 (26)	2947 (29)	1.000	2995 (29)	2995 (32)	1.000	
48	A''	—	—	—	2950 (19)	2950 (21)	1.000	2998 (20)	2998 (23)	1.000	C—H str.
50	A'	—	—	—	2993 (31)	2993 (34)	1.000	3027 (30)	3027 (33)	1.000	
51	A'	—	—	—	3000 (22)	3000 (24)	1.000	3028 (26)	3028 (29)	1.000	
52	A'	—	—	—	3012 (12)	3012 (13)	1.000	3036 (149)	3036 (16)	1.000	
53	A''	—	—	—	3028 (9)	3028 (9)	1.000	3056 (7)	3056 (7)	1.000	
54	A'	—	—	—	3029 (14)	3029 (16)	1.000	3057 (16)	3057 (18)	1.000	

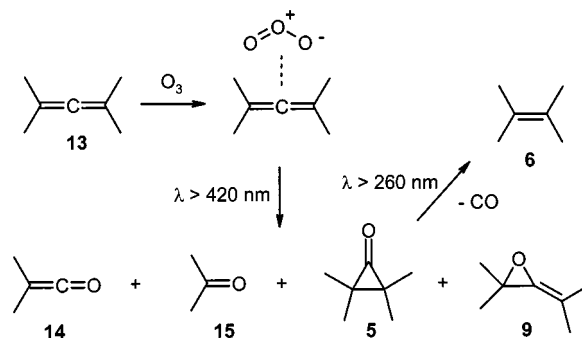
^[a] Mode-number from the ab initio calculation. IR bands with relative intensities lower than 0.5 are not tabulated. — ^[b] Relative intensity based on the strongest absorption (100%). — ^[c] The assignment is based on the comparison of the calculated and experimental spectrum and is only tentative.

was performed using ¹⁸O₃ to obtain the ¹⁸O-labelled isotopomers (Tables 1 and 2).

The co-deposition of **13** with ozone at 30 K in an argon matrix leads to a new, broad absorption in the UV/Vis spectrum with a maximum at 427 nm, which disappears after irradiation with $\lambda > 420$ nm. This absorption was assigned to the charge-transfer (CT) complex of allene **13** and ozone. A similar complex of 2,3-dimethyl-2-butene and ozone has been reported by Singmaster et al.^{[11][12]} However, IR absorptions of the CT complex of **13** and O₃ were not observed in our experiments.

The IR spectra of the products show that minor constituents of the matrix are CO (IR: 2138 cm⁻¹), CO₂ (2347 cm⁻¹), dimethylketene (**14**) (2130 cm⁻¹) and acetone (**15**) (1722 cm⁻¹). The most intense absorption in the IR spectrum of the photolysis mixture is the carbonyl absorption of cyclopropanone **5** at 1844 cm⁻¹ with an ¹⁸O isotopic shift of 36 cm⁻¹ (Table 1). Another oxidation product of **13** is allene oxide **9** with the most intense absorption at 1147 cm⁻¹ (6 cm⁻¹ ¹⁸O isotopic shift). The C—O stretching vi-

bration of the parent methylenecyclopropane **12** is found at 1109 cm⁻¹ with an ¹⁸O isotopic shift of 8 cm⁻¹.^{[7][8]} Due to the overlap with the strong Fermi-resonance absorption of **5** at 1823 cm⁻¹, the C=C stretching vibration of **9** is not observed (Table 2). On 248 nm irradiation, **5** is decarbonylated to give 2,3-dimethyl-2-butene (**6**) (Scheme 4). Thus, both



Scheme 4

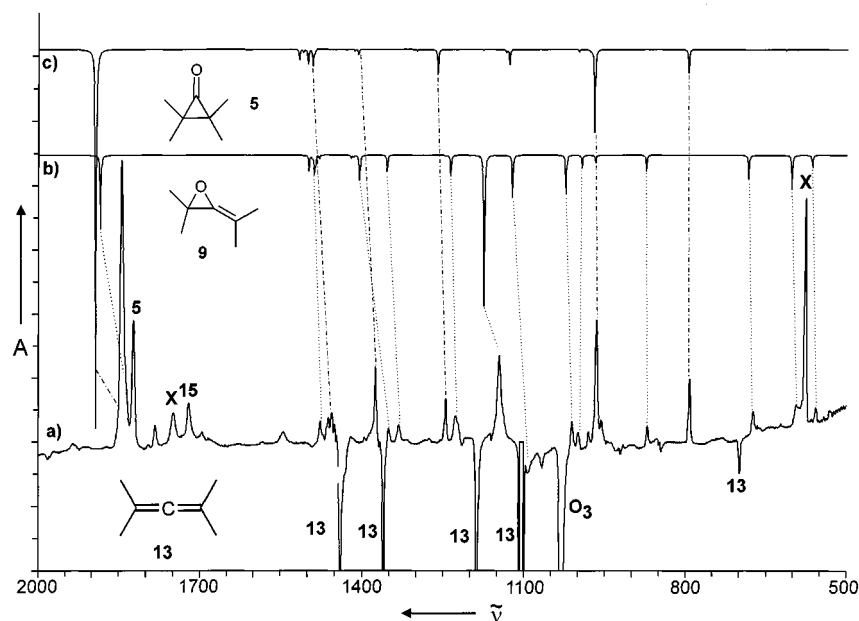


Figure 2. a) IR difference spectrum showing the oxidation of tetramethylallene **13** with oxygen atoms produced by 420 nm irradiation of 0.7% O₃ in argon at 10 K; bottom part: bands of **13** and O₃ disappearing; top part: bands of **5** and **9** appearing on irradiation; bands marked X correspond to a photolabile product of unknown constitution; b) Calculated IR spectrum of **9**; c) Calculated IR spectrum of **5**; the IR spectra were calculated at the B3LYP/6-311++G(d, p) level of theory and scaled by 0.97; the assignment of experimental and calculated IR bands is based on band positions and is only tentative, especially in areas of overlapping bands

the 193 nm photolysis of pyrazolinone **4** and the reaction of **13** with oxygen atoms result in the formation of a mixture of **5** and **9**.

Flash Vacuum Pyrolysis of Pyrazolinone 4

Pyrazolinone **4** was pyrolyzed in a quartz tube at 10^{-5} mbar and temperatures up to 1000°C, and the products

were subsequently trapped with a large excess of argon at 8–10 K. Above 650 °C pyrolysis temperature, CO is formed, indicating the decomposition of **4** (Figure 3). At 1000 °C, the pyrolysis is nearly complete, and a complex product mixture is formed with alkene **6**, ketone **8**, enol **16** as major products and cyclopropanone **5** (1844 and 1823 cm⁻¹) as one of the minor constituents.

IR absorptions of alkene **6** (1452, 1369 and 1170 cm^{-1}) and ketone **8** (1682 and 1053 cm^{-1}) were identified by com-

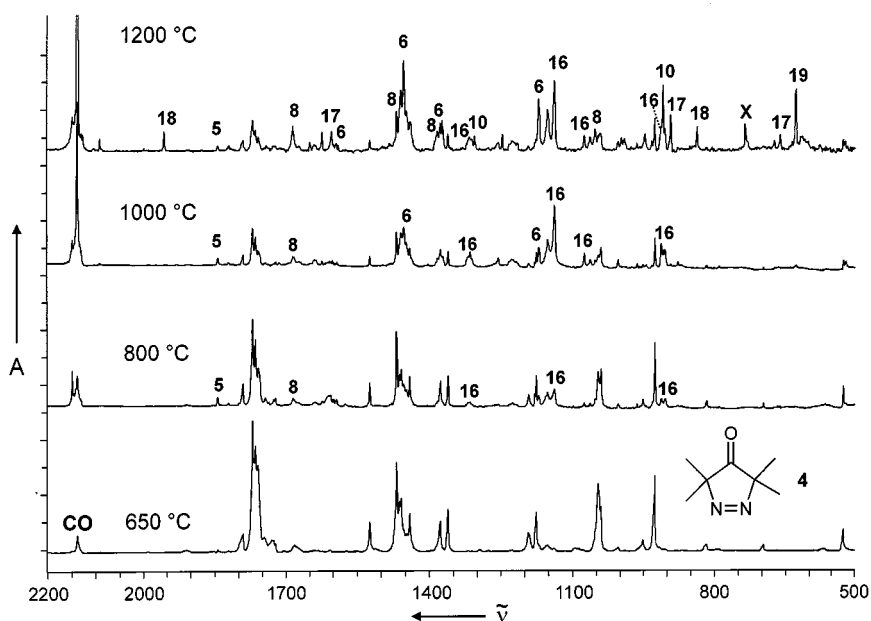
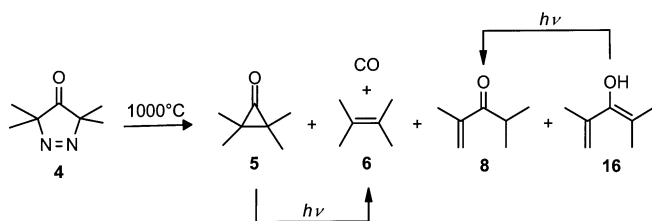


Figure 3. IR spectrum showing the pyrolysis products of **4** (alkene **6**, ketone **8**, enol **16**, and traces of cyclopropanone **5**) trapped in argon at 10 K; the pyrolyses were performed at 650, 800, 1000 and 1200 °C

Table 3. Comparison of the IR spectroscopic data of enol **16**, matrix-isolated in argon at 10 K, with calculations at the B3LYP/6-31G(d, p) (scaled by 0.97) level of theory

Nr. ^[a]	16 (¹⁶ O) argon, 10 K $\tilde{\nu}$, [cm ⁻¹]	(I _{rel}) ^[b] 16 (¹⁶ O) B3LYP/ 6-311++G(d, p) $\tilde{\nu}$, [cm ⁻¹]	(I _{rel}) ^[b] Assignment ^[c]
13	522	17	514
15	—	—	624
16	—	—	657
18	—	—	863
19	905	80	911
25	1062	42	1069
27	1152	100	1132
28	—	—	1218
29	1255	19	1240
30	1315	42	1295
35	—	—	1443
37	—	—	1451
38	—	—	1462
39	1453	23	1464
40	—	—	1467
41	1641	7	1659
42	1667	6	1696
43	—	—	2925
44	2865	25	2931
45	—	—	2949
46	—	—	2965
47	2934	20	2971
48	—	—	3003
49	—	—	3037
50	—	—	3054
51	—	—	3058
52	—	—	3065
53	—	—	3145
54	3630	49	3688

^[a] Mode-number from the ab initio calculation. IR bands with relative intensities lower than 0.5 are not tabulated. — ^[b] Relative intensity based on the strongest absorption (100%). — ^[c] The assignment is based on the comparison of the calculated and experimental spectrum and is only tentative.



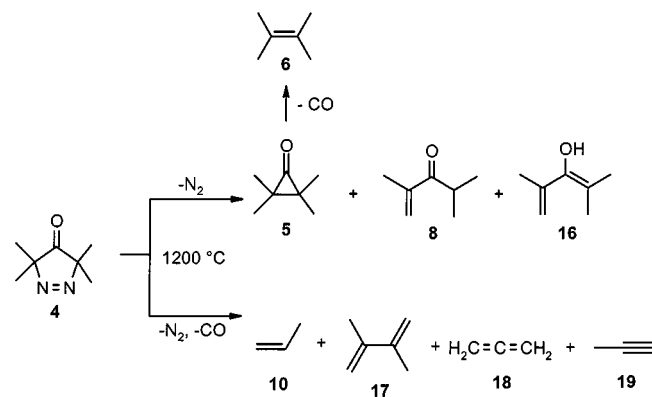
Scheme 5

parison with authentic matrix-isolated material. Enol **16** with the O–H stretching vibration at 3631 cm⁻¹ and the C=C stretching vibration at 1673 cm⁻¹ was identified by comparison of the IR spectrum with B3LYP/6-31G(d,p) calculations (Table 3). Irradiation at $\lambda = 248$ nm results in the photolysis of cyclopropanone **5** (see above) and enol **16**, which rearranges to enone **8** (Scheme 5).

Pulse Pyrolysis of Pyrazolinone **4**

Pyrazolinone **4** was thermolyzed under the conditions of pulse pyrolysis (1200°C, 2 bar, 10 ms pulse duration),^[13–15]

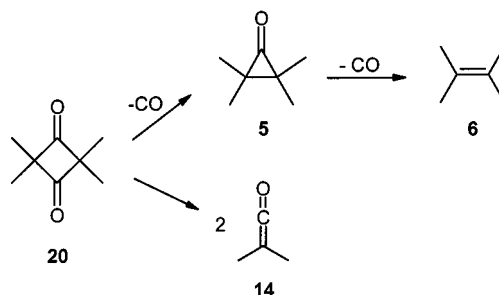
and the products were co-deposited with a large excess of argon onto a cold CsI window at 8–10 K. Again, a complex mixture of products is obtained. In addition to alkene **6**, ketone **8**, and enol **16** as the main products, traces of cyclopropanone **5**, propene (**10**) (908 and 1448 cm⁻¹), allene (**18**) (1955 cm⁻¹), propyne (**19**) (629, 1034 and 1377 cm⁻¹), and 2,3-dimethylbuta-1,3-diene (**17**) (893 and 1603 cm⁻¹) were identified by comparison with authentic matrix-isolated compounds (Scheme 6).



Scheme 6

Photolysis and Pyrolysis of Tetramethylcyclobutane-1,3-dione (**20**)

An alternative entry to cyclopropanone **5** and its isomers is the photochemical or thermal cleavage of dione **20**. The matrix photochemistry ($\lambda > 250$ nm, nitrogen at 4 K) of **20** has been investigated by Haller and Srinivasan.^[5] Loss of CO afforded cyclopropanone **5** and alkene **6** as the main products. Another major pathway is the fragmentation of **20** to give two molecules of dimethylketene **14** (Scheme 7).

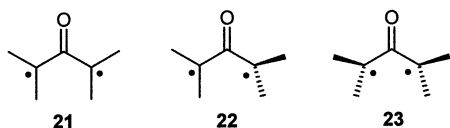


Scheme 7

Using a monochromatic light source ($\lambda = 248$ or 193 nm) and argon at 10 K, we obtained basically the same products. In addition, traces of ketone **8** were detected. FVP and pulsed pyrolysis of **20** also lead to the same product mixture as the UV photolysis. The only further product identified on FVP at 1000°C was enol **16** (trace amounts), which rearranges to ketone **8** upon irradiation at $\lambda = 248$ nm.

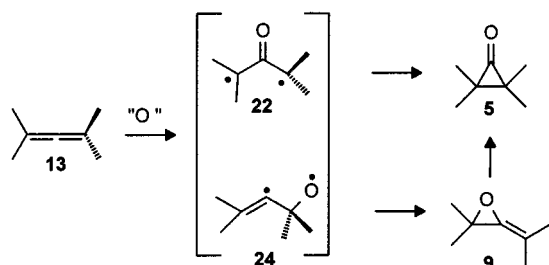
Discussion

Pyrazolinone **4** represents a bichromophoric substrate, i.e., it contains both azo and carbonyl groups for photolytic excitation. Conventional long wavelength ($\lambda > 250$ nm)^[1a] and short wavelength UV (185 nm)^[1b] photolyses lead preferentially to denitrogenation, although azine **7** is also formed in 15–37% yield. Irradiation with $\lambda = 193$ nm produces mainly cyclopropanone **5** and small amounts of allene oxide **9** with only trace amounts of the azine **7**. A plausible precursor of **5** and **9** may be an oxyallyl, which can either form a C–C bond as in **5** or a C–O bond as in **9** (Scheme 8). Such oxyallyls have been postulated several times as intermediates in the allene oxide–cyclopropanone isomerization process,^[16] but as yet have never been directly observed. The IR spectrum of the planar diradical **21** was calculated by Borden et al.,^[17] however, in our experiments, no IR absorptions could be assigned to **21**.



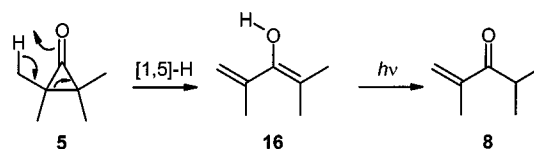
Scheme 8

The electrophilic addition of oxygen atoms [$O(^3P)$] to allene (**18**) has been investigated by Hammond et al. using ab initio theory.^[18] Two reaction pathways are calculated. In the first, O-atom attack at the central carbon atom of allene is followed by ring closure of the initially produced parent orthogonal oxyallyl diradical to cyclopropanone **5**. The energy barrier for this reaction was found to be 1.8 kcal/mol lower than that of the reaction initiated by attack at the terminal carbon atom. In the second pathway, the intermediate is the parent allenoxyl diradical which subsequently cyclizes to allene oxide (**12**). However, the formation of both cyclopropanone and allene oxide as products of the oxygen transfer to allene in cryogenic matrices suggests that both pathways are important.^[7–9] This is in agreement with our observation of the oxygen transfer to **13**, which produces both **5** and **9**.

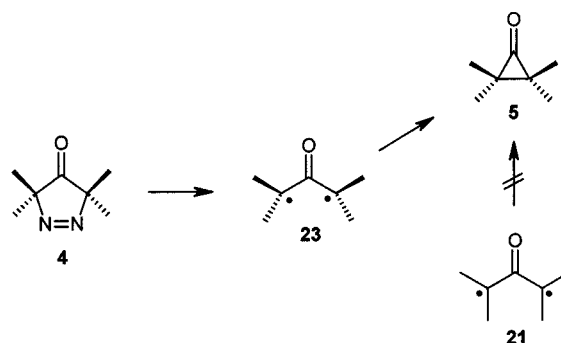


Ketone **8** is presumably formed by rearrangement of cyclopropanone **5**. The first step is a [1,5]-H migration in **5** which results in the ring-opening and formation of enol **16**. Since enol **16** is labile towards UV irradiation (248 nm), it

is only observed as a product of the thermolysis but not of the photolysis of **4**.



In this study, we were able to generate and characterize allene oxide **9** and enol **16** for the first time by the photolysis and thermolysis, respectively, of pyrazolinone **4**. Although tetramethyloxyallyl probably is a key intermediate in the transformations leading to **5** and **9**, this diradical could not be detected in our experiments. Obviously, the ring-closure to cyclopropanone **5** is rapid under the experimental conditions. Nitrogen loss of **4** results in **23** with the methyl groups at the radical centers rotated out of plane. To avoid the ring closure, the more stable planar **21** has to be directly generated from a suitable precursor.



Experimental Section

Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Messer-Griesheim, 99.9999%) on top of a CsI window at a rate of approximately 0.15 mmol/min. Pyrazolinone **4** was matrix-isolated by sublimation at -20°C and deposition with a large excess of argon on top of a cold window (30 K). Infrared spectra were recorded with a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of $400\text{--}4000\text{ cm}^{-1}$.

Irradiations were carried out with a KrF ($\lambda = 248$ nm) or ArF Excimer Laser ($\lambda = 193$ nm; Lambda Physik COMPex 100) or Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the arc lamps was absorbed by a 10 cm path of water. Schott cut-off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

Pyrolyses were carried out in a quartz tube placed 3 cm in front of the cold window. In order to obtain short contact times, a heating zone of only 3 cm was used. A large excess of argon and the precursor were allowed to pass through the pyrolysis zone and the products were directly trapped on top of the cold window at 10 K.

The pulsed deposition unit was constructed similar to Chen's^[13] and Maier's^{[14][15]} description. We used a valve supplied by GEN-

ERAL VALVE Corporation, with an orifice of 0.5 mm diameter. The valve was connected to an alumina tube of 2 mm inner diameter, which was mounted on a second alumina tube with 1 mm inner diameter, each tube having a length of 30 mm. The latter tube can be heated to 1400 °C by means of a tantalum wire. The distance between the orifice and the spectroscopic window was 30 mm. For the use of pressures higher than 1 bar, the gas mixtures were prepared in a stainless-steel gas mixing unit.

Pyrazolinone **4** was prepared by the procedure described by R. J. Crawford et al.^[20]

Calculations were performed with the Gaussian 94 program package.^[21] Geometries and vibrations were calculated at the MP2/6-31G, B3LYP/6-31G(df) or the B3LYP/6-311G(3df,3pd) level of theory.^[22] The calculated geometries of **5**, **9**, and **16** are included in the Supporting Information.

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