121. Thermal Rearrangement of 5,6-Epimino-5,6-dihydro-β-ionone and Derivatives

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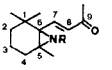
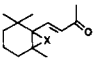
Thermolysis of 5,6-epimino-5,6-dihydro-β-ionone (**1**) and its *N*-methyl derivative (**2**) leads to their monocyclic isomers **6** and **10**, respectively, presumably due to a direct [1,5]-H shift; on prolonged heating, these isomers are converted easily into pyrrole derivatives. In contrast, the thermoisomer **12** resulting from 5,6-(*N*-methoxycarbonyl)epimino-5,6-dihydro-β-ionone (**3**) by the same mechanism, does not undergo further ring transformation, but equilibrates with its more stable tautomer **13**.

Introduction. – In the last few years, the thermal behavior of aziridines has been studied in great detail [1]. Monocyclic vinylaziridines have been shown to convert by *conrotatory* ring opening into azomethin ylides or by [1,5]-H shift into acyclic imines depending on the structure and the substituents on the N-atom [2]. In the same manner, bicyclic vinylaziridines bridged on C(2) and C(3) of the heterocycle yield thermolytic products which were due to *disrotatory* ring opening, forming intermediary cyclic azomethin ylides, or to a [1,5]-H shift [3]. The kind of the substituent on the N-atom and the presence of other substituents that stabilize the azomethin ylide by conjugation appear to be decisive for the course of the reaction.



1 R=H
2 R=CH_3
3 R=CO_2CH_3



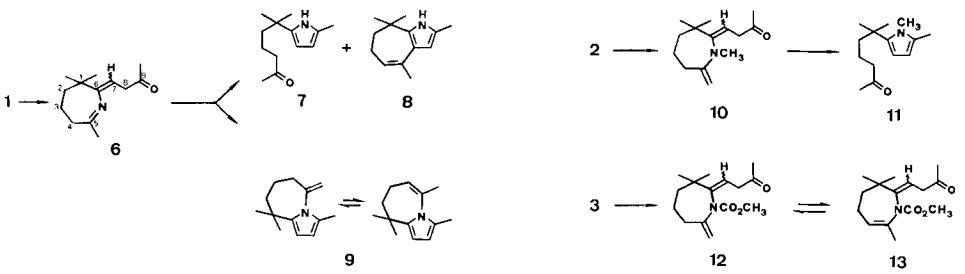
4 X=O
5 X=CH_2

Due to their structure, 5,6-epimino-5,6-dihydro-β-ionone (**1**)[1]) and its *N*-substituted derivatives **2** and **3** are to be considered to belong to the latter type. The aim of the present investigation was to examine the thermal behavior of these compounds and to compare the results with those obtained from thermolysis of the epoxy- and methano-analogous compounds **4** [5] and **5** [6].

Results. – If a solution of **1** in dry CD_3CN is heated under Ar at 130°, the appearance of new signals in the ^{1}H-NMR can be observed after 30 min already. During further heating at this temperature, these signals increase while the signals of **1** decrease at the same time. After 9 h, it is virtually impossible to detect **1** by ^{1}H-NMR. The initially simple ^{1}H-NMR spectrum is getting more complex with prolonged reaction time because **6**, the

[1]) In ionone derivatives, numbering according to the carotenoid nomenclature is used [4].

Scheme 1



first thermolysis product observed, is converted further into pyrrole **7** and other unidentified compounds *(Scheme 1)*.

A solution of **1** in dry C_6D_6 shows the same reaction upon heating at 130°. From an integration of the respective signals in the ^{1}H-NMR spectrum, it can be derived that after 3 h in CD_3CN and 6 h in C_6D_6 a 50% conversion is reached. The thermolysis product **6** could not be isolated: after flash chromatography, only compounds **7–9** were eluted as artefacts produced by the contact with silica gel.

Therefore, the structure of **6** is based mainly on the ^{1}H-NMR and ^{13}C-NMR spectra of the thermolysis solution (see *Table*). The structures of pyrrole **7** and of the bicyclic compounds **8** and **9** were clearly proved by the analytical data (see *Exper. Part*).

Table. *NMR-Data of Compounds* **6**, **10**, **12** *and* **13**[a])

	6[b])	**10**[b])	**12**[b])	**13**[c])
H–C(7)	4.88 (J = 7)	5.47 (J = 7)	5.80 (J = 7)	5.69 (J = 7)
H–C(8)	2.92 (J = 7)	3.06 (J = 7)	3.00 (J = 7)	3.11 (J = 7)
H_2C=C(5)	–	3.26; 3,41	4.55; 5.38	–
H–C(4)	–	–	–	5.08 (J = 5)
CH_3	1.01; 2.00	1.08; 1.22; 2.04; 2.74 (CH_3N)	0.98; 1.20; 2.02; 3.53 (CH_3O)	1.11; 1.18; 1.99; 2.11; 3.66 (CH_3O)
CH_2	1.00–2.30	1.00–2.30	1.00–2.35	1.10–2.25
C(1)	36.41	40.81	40.17	40.65
C(2)	34.55	34.44	35.04	38.86
C(3)	19.88	25.73	24.43	23.76
C(4)	44.18	43.93	43.45	117.65[d])
C(5)	171.90[d])	153.22[d])	145.59[d])	137.21[d])
C(6)	157.98[d])	156.90[d])	148.03[d])	149.27[d])
C(7)	101.18	115.80	120.40	121.12[d])
C(8)	42.32	43.04	42.39	42.50
C(9)	207.83	207.13	206.29	206.05
CH_2=C(5)	–	77.01	99.42	–
CH_3	27.99; 29.65	26.15; 29.81; 29.90; 41.30 (CH_3N)	26.93; 28.88; 29.93 52.83 (CH_3O)	27.61; 29.68; 52.47 (CH_3O)
CO_2	–	–	157.81	154.12

[a]) ^{1}H-NMR recorded at 100 MHz, ^{13}C-NMR at 25,16 MHz; δ [ppm], coupling constants in Hz; atom numbering as indicated in *Formula* **6**.

[b]) CD_3CN.

[c]) $CDCl_3$.

[d]) Assignments may be interchanged.

Most important of the NMR data of **6** are the *d* at 2.92 ppm (J = 7) of 2H–C(8)[2]) and the *t* at 4.88 ppm (J = 7) of H–C(7), which together with the corresponding *t* at 42.32 ppm of C(8), *d* at 101.18 ppm of C(7), and *s* at 207.83 ppm of C(9) prove the newly formed homoconjugated ketone; in addition 2*s* at 157.98 and 171.90 ppm of C(5) and C(6) as well as 3*t*, 1*s*, and the overlapping *q* of the CH_3 groups are observed which confirm the structure beyond any doubt.

If the H-atom of the aziridine N-atom is replaced by a CH_3 group[3]), the thermal stability is reduced drastically: in dry CD_3CN or C_6D_6, within 60 min at 80 or 90°, respectively, **2** is completely and according to ^{1}H-NMR uniformly rearranged to **10**. This compound too is not stable during further heating and is converted into a pyrrole derivative: after 3 h, only signals of **11** can be detected by ^{1}H-NMR.

Compound **10** is extremely sensitive to moisture and could not be isolated. Evidence for its structure was gathered from the ^{1}H-NMR and ^{13}C-NMR spectra of the thermolysis solution. The structure of the isolable pyrrole derivative **11** is confirmed by the analytical data (see *Exper. Part*).

As characteristic signals in the ^{1}H-NMR of **10**, the *d* at 3.06 (J = 7) and the *t* at 5.47 ppm (J = 7) of the homoconjugated ketone side chain as well as the *s* at 3.26 and 3.41 ppm of the exocyclic methylidene group should be mentioned, in the ^{13}C-NMR the *t* at 77.01 (CH_2=C(5)), the *d* at 115.80 (C(7)), and the *s* at 156.90 and 153.22 ppm (C(5) and C(6)), whose chemical shifts and multiplicities are in good agreement with expected values.

As compared to **1**, thermolysis of the *N*-acylated compound **3** is also facilitated: at 125°, a solution of **3** in dry CD_3CN reacts within 6 h completely and without the formation of any by-products that are detectable by ^{1}H-NMR to give **12.** Further heating does not lead to a pyrrole derivative but by a slow reaction to its tautomer **13**. After 58 h, a 1:3 ratio of **12**/**13** can be estimated by ^{1}H-NMR; this ratio does not change on further heating.

Compounds **12** and **13** are not hydrolyzed so easily and, therefore, can be isolated. An attempted separation of the tautomers by liquid chromatography (LC) was not successful. The spectral data of **12** were obtained from a thermolysis solution which did not show any isomer in the NMR; the spectral data of **13** were determined with a 3:1 mixture **13**/**12** (see *Table*).

Among the ^{1}H-NMR data of **12**, particular characteristic signals are the *d* at 3.00 (J = 7) and the *t* at 5.80 ppm (J = 7), furthermore the 2*s* at 4.55 and 5.38 ppm of H_2C=C(5), which, taken together with the corresponding signals in the ^{13}C-NMR (*t* at 99.42, *d* at 120.40, and 2*s* at 145.59 and 148.03 ppm) prove the structure.

The ^{1}H-NMR data of **13** were essentially the same, the only distinctive feature being the br. *s* of a CH_3 group at 1.99 ppm and the br. *t* at 5.08 ppm of H–C(4) as well as the 2*d* at 117.65 and 121.12 ppm of the H-bearing olefinic C-atoms in the ^{13}C-NMR.

Cycloaddition Experiments. – The structures of the thermolytic products **6**, **10**, and **12** do not permit to decide whether isomerization comes along by a direct [1,5]-H shift or whether previously formed cyclic azomethin ylides react to the product by subsequent H shift (see below, *Scheme 3*). It was hoped to obtain further information on the mechanism from thermolysis of **1**–**3** in the presence of dimethyl acetylenedicarboxylate (DMAD): as recently reported by several groups [3] [8], this reactive dipolarophile adds very well to cyclic azomethin ylides even at low temperature.

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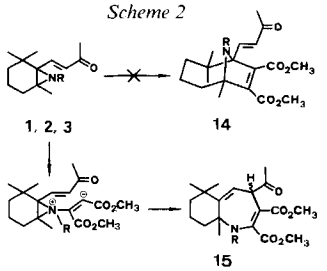
[2]) For numbering, see the *Table, Footnote a.*

[3]) Whereas **1** can not be methylated on the N-atom by the usual alkylating agents [7], the use of methyl fluorosulfonate brings about an almost complete reaction.

Scheme 2

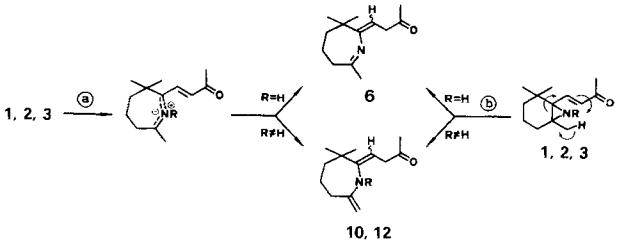


In the experiments performed with **1–3**, numerous products were formed which could not be separated and isolated. According to the ^{1}H-NMR spectra of the crude mixtures, however, the formation of azomethin-DMAD cycloaddition products of structure **14** *(Scheme 2)* can be ruled out, since the characteristic *d*'s of the enone side chain were not apparent. The thermolytic products **6**, **10**, and **12**, respectively, also could not be detected. Presumably, these results can be rationalized by an initial addition of DMAD to the aziridine N-atom, and subsequent formation of complex mixtures, which according to literature results (*cf.* [3] [9]) are likely to contain compounds of structure **15**.

In a further experiment, a CD_3CN solution of **1** containing the less reactive dimethyl maleate was heated. In this case likewise, no cycloaddition products could be found. As indicated by ^{1}H-NMR, the thermolysis proceeds undaunted by the presence of the dipolarophile.

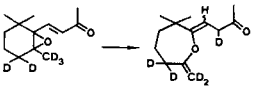
Discussion. – The structures of the compounds determined in the thermolysis solutions prove that bicyclic ionone-type aziridines do react under cleavage of the C(5),C(6) bond; products that lead to the conclusion that a C,N-bond cleavage has taken place

Scheme 3



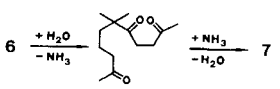
could not be found. A possible mechanism of this reaction may be a disrotatory opening of the aziridine ring whereby a cyclic azomethin ylide is formed, followed by a H shift (*Path a*) or a direct [1,5]-H shift *(Path b, Scheme 3)*; a homolytic cleavage of the C,C bond – for which, to my knowledge, there is no experimental proof – was not taken into consideration. An argument against *Path a* is, that it was not possible to obtain trapping products with DMAD or dimethyl maleate. *Path b* is supported by the results of the thermolysis of the O- and C-analogues **4** and **5**, respectively: the isotope effect found in the isomerization of (D_5)-**4**- to (D_5)-**16** confirms the direct [1,5]-H shift [5] *(Scheme 4)*; the fact that the thermolysis products of the N-, O- and C-analogous compounds correspond to each other suggests formation of the products by the same pathway.

Scheme 4



(D$_5$)-**4** (D$_5$)-**16**

Scheme 5



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The formation of pyrrole **7** in the subsequent course of thermolysis may be explained by the effect of catalytic amounts of H_2O: hydrolysis converts **6** into ammonia and **17**, which in turn condense easily to **7** (*Scheme 5; Paal-Knorr* synthesis); the additionally found bicyclic pyrroles **8** and **9** are supposed to be condensation products formed by silica-gel catalysis in the course of LC. The same mechanism also explains the formation of pyrrole **11** from **10** during prolonged heating. The enamide derivatives **12** and **13**, less sensitive to hydrolysis, however, do not show any tendency to pyrrole formation during the reaction time.

Conclusions. – The present study shows that the course of the thermolytic reaction of 5,6-epimino-5,6-dihydro-β-ionone (**1**) and the *N*-substituted derivatives **2** and **3** is the same as that of the 7-oxa and 7-carba analogues **4** [5] and **5** [6], respectively. The thermolysis of the aziridine derivatives occurs at the lowest temperature, whereas the oxirane derivatives require the highest temperature. Thus, similar differences in stability were found in the ionone series as the ones existing in *cis*-divinyl-substituted cyclopropanes, oxiranes, and aziridines [10] as well as in *cis*-bicyclo[6.1.0]nonadienes and their 9-oxa and 9-aza analogues [11].

The elemental analyses and NMR and mass spectra were carried out by the analytical department of the ETHZ. The author is indebted to the following persons for their help: Miss *B. Brandenberg*, Mr. *F. Fehr* and Mr. *M. Langenauer* (NMR), Mrs. *L. Golgowski* and Prof. *J. Seibl* (MS), and Mr. *D. Manser* (elemental analyses).

Experimental Part

1. *General.* See [12].

2. *5,6-(*N*-Methylepimino)-5,6-dihydro-β-ionone* (= *(3*E*)-4-(1,2-(*N*-Methylepimino)-2,6,6-trimethylcyclohexyl)-3-buten-2-one*; **2**). A soln. of 1.23 g (10.8 mmol) of methyl fluorosulfonate in 2 ml of abs. benzene was added with stirring and ice/H_2O cooling to a soln. of 2.13 g (10.3 mmol) of **1** in 20 ml of abs. benzene. After 30 min, the mixture was diluted with 15 ml of pentane, and the separating **2**·$HOSO_2F$ was filtered off and washed with pentane: 2.69 g (81%) of brownish crystals, m.p. > 50° (dec.). IR($CHCl_3$): 2950*s* (br.), 1695*s*, 1670*s*, 1620*s*, 1250*s*. ^{1}H-NMR: 1.10, 1.20, 1.48 (3*s*, 2CH_3–C(1), CH_3–C(5)); 1.0–2.4 (br. *m*, CH_2(2), CH_2(3), CH_2(4), NH); 2.38 (*s*, CH_3–C(9)); 2.82 (*d*, J = 4, after D_2O exchange *s*, CH_3N); 6,52 (*AB*, δ_A = 6.37 δ_B = 6.67, J = 17, H–C(7), H–C(8)).

The base was obtained by alkalinizing a H_2O soln. of **2**·$HOSO_2F$ with 2N NaOH and extracting the soln. with CH_2Cl_2. Drying and evaporation of the org. layer afforded a slightly yellow oil which crystallized in the cold: 1.80 g of **2**, after recrystallization from pentane, colorless crystals, m.p. 80°, b.p. 120°/0.05 Torr. UV (0.535 mg in 10 ml of pentane): 223 (11600), 274 (1150). IR: 3030*w*, 2990*m* (sh), 2950*s*, 2860*s*, 2800*w*, 1690*s*, 1670*s*, 1615*s*, 1455*m*, 1430*m* (sh), 1370*m*, 1350*s*, 1275*m*, 1240*s*, 1165*m*, 1120*m*, 975*m*. ^{1}H-NMR: 0.90, 0.97, 1.01 (3*s*, 2 CH_3–C(1), CH_3–C(5)); 1.00–2.20 (br. *m*, CH_2(2), CH_2(3), CH_2(4)); 2.20 (*s*, CH_3–C(9)); 2.25 (*s*, CH_3N); 6.08 (*d*, J = 16, H–C(8)); 6.68 (*d*, J = 16, H–C(7)). ^{13}C-NMR: 16.51, 25.79, 26.80, 27.04, (4*q*, 2 CH_3–C(1), CH_3–C(5), CH_3–C(9)); 17.54 (*t*, C(3)); 31.93 (*t*, C(4)); 33.49 (*q*, CH_3N); 34.09 (*s*, C(1)); 35.64 (*t*, C(2)); 43.33 (*s* C(5)); 52.59 (*s*, C(6)); 136.67 (*d*, C(8)); 141.22 (*d*, C(7)); 196.85 (*s*, C(9)). MS: 221 (22, M^+, $C_{14}H_{23}NO$), 206(28), 179(14), 178(100), 176(18), 164(26), 152(13), 150(36), 149(11), 148(26), 137(10), 136(72), 135(24), 134(15), 124(12), 123(28), 122(45), 121(14), 120(15), 110(18), 109(22), 108(44), 107(19), 98(12), 96(19), 95(20), 94(15), 93(12), 91(17), 84(29), 82(21), 81(14), 79(21), 77(16), 71(62), 70(12), 69(22), 68(26), 67(17), 57(12), 56(94), 55(29), 53(17), 43(73), 42(31), 41(47). Anal. calc. for $C_{14}H_{23}NO$ (221.33): C 75.97, H 10.47, N 6.33; found: C 76.00, H 10.40, N 6.44.

3. *Thermolysis of* **1**. 3.1. *^{1}H-NMR Control.* A soln. of 90.9 mg (0.44 mmol) of **1** in 0.25 ml of dry CD_3CN was sealed in a NMR tube under Ar and heated in an oil bath at 130°. After regular intervals, the tube was taken out from the oil bath, cooled under running H_2O and measured. The signals of **1** had disappeared after 9 h; according to its ^{1}H-NMR, the soln. contained a mixture of **6** (main portion), **7**, and other unidentified compounds. *4-(3,4,5,6-Tetrahydro-3,3,7-trimethyl-2*H*-azepin-2-yliden)-2-butanone* (**6**): ^{1}H-NMR, ^{13}C-NMR: see *Table*.

The thermolysis of **1** in dry C_6D_6 under the same conditions gave a similar result: after 12 h at 130°, the ^{1}H-NMR showed signals of **6** (main product), **7**, and other unidentified products.

3.2. *Isolation of* **7–9**. A soln. of 600 mg (2.9 mmol) of **1** in 0.5 ml of abs. CH_3CN was sealed under Ar in a *Pyrex* tube and heated for 5 h at 130°. Chromatography (Et_2O/petroleum ether 40–60° 3:1) gave 350 mg (65%) of **7** and 170 mg (31%) of a mixture containing **8** and minor amounts of **9**. A second LC of the mixed fraction (Et_2O/petroleum ether 40–60° 1:1) yielded **8** and **9**. *6-(5-Methyl-2-pyrrolyl)-6-methylheptan-2-one* (**7**): Colorless oil, b.p. 130°/0.03 Torr. UV (2.499 mg in 20 ml of pentane): 229 (5070). IR: 3470*m*, 3380*m* (br.), 3100*w*, 2960*s*, 2920*s* (sh), 2860*m*, 1710*s*, 1580*w*, 1490*w*, 1450*m*, 1405*m*, 1375*m*, 1360*s*, 1305*w*, 1265*m*, 1215*m*, 1170*m*, 1150*m*, 1025*m*. ^{1}H-NMR: 1.22 (*s*, 2 CH_3–C(6)); 1.35–1.60 (*m*, *t*-like, CH_2(4), CH_2(5)); 2.17 (*s*, CH_3–C(2)); 2.23 (*s*, CH_3–C(5')); 2.32 (*m*, CH_2(3)); 5.74 (*d*, *J* = 3, after D_2O exchange *s*, H–C(3'), H–C(4')); 8.00 (br. *s*, D_2O exchange, NH). ^{13}C-NMR: 12.95 (*q*, *C*H_3–C(5')); 19.34 (*t*, C(4)); 28.29 (*q*, 2*C*H_3–C(6)); 29.49 (*q*, *C*H_3–C(2)); 34.32 (*s*, C(6)); 42.73, 43.75 (2*t*, C(3), C(5)); 103.38, 105.10 (2*d*, C(3'), C(4')); 125.70 (*s*, C(5')); 138.42 (*s*, C(2')); 209.63 (*s*, C(2)). MS: 208 (8, M^+, $C_{13}H_{21}NO$), 134(12), 122(100), 43(13). Anal. calc. for $C_{13}H_{21}NO$ (207.32): C 75.32, H 10.21, N 6.76; found: C 75.15, H 10.38, N 6.72.

*7,8-Dihydro-2,4,8,8-tetramethyl-6*H*-cyclohepta[*b*]pyrrole* (**8**). Colorless, air-sensitive crystals, m.p. 63°, b.p. 100°/0.05 Torr. UV (0.423 mg in 5 ml of pentane): 232 (7000), 264 (5400). IR: 3480*s*, 3390*m*, 3100*w*, 2960*s*, 2920*s*, 2870*s*, 1635*s*, 1575*w*, 1495*w*, 1455*m* (sh), 1440*s*, 1385*m*, 1370*m*, 1350*m*, 1285*w*, 1225*w*, 1170*m*, 1010*w*. ^{1}H-NMR: 1.25 (*s*, 2CH_3–C(8)); 1.70 (*m*, CH_2(7)); 1.97 (*d*, *J* = 1.5, CH_3–C(4)); 2.20 (*s*, CH_3–C(2)); 2.30 (*m*, CH_2(6)); 5.41 (*tq*, *J* = 6, 1.5, H–C(5)); 5.81 (*d*, *J* = 3, after D_2O exchange *s*, H–C(3)); 8.60 (br. *s*, D_2O exchange, NH). ^{13}C-NMR: 12.77 (*q*, *C*H_3–C(2)); 24.03 (*q*, *C*H_3–C(4)); 25.67 (*t*, C(7)); 30.32 (*q*, 2*C*H_3–C(8)); 35.68 (*s*, C(8)); 39.82 (*t*, C(6)); 105.54 (*d*, C(3)); 118.30 (*s*, C(3a)); 122.37 (*d*, C(5)); 124.22 (*s*, C(2)); 129.64 (*s*, C(8a)); 135.43 (*s*, C(4)). MS: 189 (44, M^+, $C_{13}H_{19}N$), 175(14), 174(100), 160(10), 159(16), 158(14), 146(23), 145(14), 144(15), 132(10). Anal. calc. for $C_{13}H_{19}N$ (189.30): C 82.48, H 10.12, N 7.40; found: C 80.94, H 9.95, N 7.09.

*5,6-Dihydro-1,4,4,8-tetramethyl-4*H*-pyrrolo[1,2-a]azepine* (**9a**)/*5,6,7,8-Tetrahydro-1,4,4-trimethyl-8-methyliden-4*H*-pyrrolo[1,2-a]azepine* (**9b**). Ratio **9a**/**9b** 3:2 (^{1}H-NMR). Colorless oil, b.p. 90/0.05 Torr. UV (0.566 mg in 5 ml of pentane): 243 (5500). IR: 3100*w*, 3040*w*, 2960*s*, 2920*s*, 2860*s*, 1660*m*, 1640*m*, 1500*w*, 1435*m*, 1395*s*, 1380*m* (sh), 1355*m*, 1330*m*, 1310*m*, 1275*m*, 1260*m*, 1210*w*, 1175*w*, 1120*w*, 1020*w*. ^{1}H-NMR: 1.24 (*s*, 2CH_3–C(4)); 2.09 (br. *s*, CH_3–C(8)); 2.20 (*s*, CH_3–C(1)); 5.64 (*m*, H–C(7)) (signals of **9a**); 1.26 (*s*, 2CH_3–C(4)); 2.14 (*s*, CH_3–C(1)); 4.80, 5.16 (2*s*, CH_2=C(8)) (signals of **9b**); 1.3–2.4 (structured *m*, CH_2) and 5.79 (*s*, pyrrol H-atoms) (signals of both tautomeres superimposed). ^{13}C-NMR[4]): 21.50 (*q*, *C*H_3–C(8)); 122.43 (*d*, C(7)) (signals of **9a**): 110.72 (*t*, *C*H_2=C(8)) (signal of **9b**). MS: 189 (36, M^+, $C_{13}H_{19}N$), 175(14), 174(100), 160(15), 159(13), 149(20), 145(12), 144(11).

4. *Thermolysis of* **2**. 4.1. *^{1}H-NMR Control.* Sample preparation and procedure as described in *3.1;* bath temp. 80°. After 60 min, the ^{1}H-NMR showed only signals of *4-(1,3,3-Trimethyl-7-methylidenazepan-2-yliden)-2-butanone* (**10**). ^{1}H-NMR, ^{13}C-NMR: see *Table*. During further heating for 2 h, **10** was converted completely to **11**. Thermolysis of **2** in C_6D_6 at 90° gave the same result.

4.2. *Isolation of* **11**. A soln. of 440 mg (2 mmol) of **2** in 5 ml of dry CH_3CN was refluxed under Ar for 12 h. After evaporation, the residue was purified by LC (Et_2O/petroleum ether 40–60° 1:1): 400 mg (90%) of *6-(1,5-Dimethyl-2-pyrrolyl)-6-methylheptan-2-one* (**11**), colorless oil, b.p. 125°/0.05 Torr. UV (1.012 mg in 10 ml of pentane): 225 (6300). IR: 3100*w*, 2970*s*, 2930*s* (sh), 2900*s* (sh), 2860*m*, 1715*s*, 1490*w*, 1460*m*, 1425*m*, 1390*s*, 1360*s*, 1300*m*, 1240*w*, 1160*m*, 1020*w*. ^{1}H-NMR: 1.30 (*s*, 2CH_3–C(6)); 1.20–1.75 (br. *m*, CH_2(4), CH_2(5)); 2.05 (*s*, CH_3–C(2)); 2.15 (*s*, CH_3–C(5')); 2.31 (*t*, *J* = 7, CH_2(3)); 3.50 (*s*, CH_3N); 5.75 (*m*, *s*-like, H–C(3'), H–C(4')). ^{13}C-NMR: 12.95 (*q*, *C*H_3–C(5')); 19.45 (*t*, C(4)); 28.71 (*q*, 2*C*H_3–C(6)); 29.72 (*q*, *C*H_3–C(2)); 32.53 (*q*, CH_3N); 35.15 (*s*, C(6)); 40.91, 43.81 (2*t*, C(3), C(5)); 104.51, 104.81 (2*d*, C(3'), C(4')); 129.46 (*s*, C(5')); 138.43 (*s*, C(2')); 208.73 (*s*, C(2)). MS: 221 (10, M^+, $C_{14}H_{23}NO$), 137(11), 136(100). Anal. calc. for $C_{14}H_{23}NO$ (221.33): C 75.97, H 10.47, N 6.33; found: C 75.92, H 10.47, N 6.33.

5. *Thermolysis of* **3**. 5.1. *^{1}H-NMR Control.* For sample preparation and procedure, see *3.1;* bath temperature 125°. After 3 h, only signals of **12** could be detected in the ^{1}H-NMR; during further heating at 125°, signals of **13** appeared.

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[4]) Only the signals defining the structure of the tautomer are quoted.

5.2. *Isolation of* **12** *and* **13**. A soln. of 108 mg (0.4 mmol) of **3** in 0.25 ml of abs. CH_3CN was sealed under Ar in a *Pyrex* tube and heated at 125° for 58 h. After evaporation, the residue was distilled affording 92 mg (85%) of mixture of *methyl 2,3,4,5-tetrahydro-3,3,7-trimethyl-2-(3-oxobutyliden)-1H-azepine-1-carboxylate* (**13**) and *methyl 3,3-dimethyl-7-methylen-2-(3-oxobutyliden)azepane-1-carboxylate* (**12**) as a colorless oil, b.p. 145°/0.03 Torr, in the ratio 3:1 (^{1}H-NMR). IR: 3030*w* (sh), 2960*m*, 2920*m*, 2860*m* (sh), 1715*s*, 1665*m*, 1620*w*, 1435*m*, 1375*m*, 1360*m*, 1320*s*, 1225*m*, 1185*m*, 1150*m*, 1080*m*. ^{1}H-NMR, ^{13}C-NMR: see *Table*. MS: 265 (3, M^+, $C_{15}H_{23}NO_3$), 222(26), 208(32), 207(100), 194(20), 192(46), 180(40), 166(62), 152(58), 150(22), 147(33), 133(28), 107(32), 79(24), 59(20), 56(56), 55(26), 54(21), 53(24), 43(74), 41(44), 39(24).

Reaction of **1** *with Dimethyl Acetylendicarboxylate (DMAD)*. To a soln. of 101 mg (0.49 mmol) of **1** in 0.25 ml of dry CD_3CN previously cooled to −10°, were added 137 mg (0.96 mmol) of DMAD. On warming up to r.t., the soln. became dark brown. ^{1}H-NMR: no evidence of cycloaddition products of structure **14** in the soln. TLC: at least 5 products.

Reaction of **2** *with DMAD*. A soln. of 200 mg (0.90 mmol) of **2** and 257 mg (1.8 mmol) of DMAD in 0.5 ml of dry CD_3CN was sealed under Ar in a NMR tube and heated at 90° for 30 min. ^{1}H-NMR: the deep brown soln. did not show the characteristic *d* of an enone side chain, no evidence of cycloaddition products of structure **14**.

Reaction of **3** *with DMAD*. A soln. of 172 mg (0.65 mmol) of **3** and 184 mg (1.3 mmol) of DMAD in 0.3 ml of dry CD_3CN was sealed under Ar in a NMR tube. After heating at 120° for 4 h, the ^{1}H-NMR signals of **3** had disappeared and no evidence of cycloaddition products of structure **14** was present.

Thermolysis of **1** *in the Presence of Dimethyl Maleate*. A soln. of 102 mg (0.49 mmol) of **1** and 71 mg (0.49 mmol) of dimethyl maleate in 0.25 ml of dry CD_3CN was sealed under Ar in a NMR tube and heated at 120° for 8 h. As monitored by ^{1}H-NMR, the reaction proceeded as it does in absence of dimethyl maleate.

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