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THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF 3,5-DIVINYLSUBSTITUTED 1-PYRAZOLINES[1].

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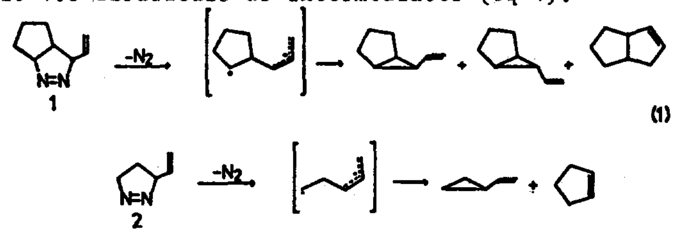
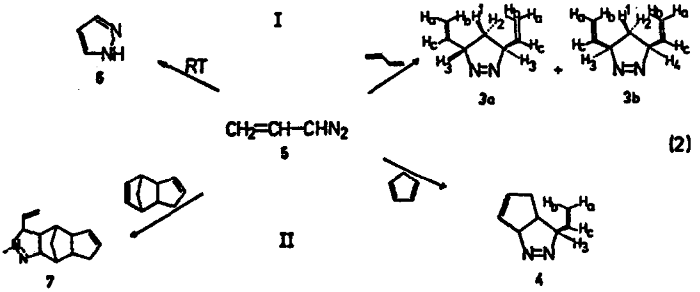
We recently reported data on the thermal and photochemical decomposition of exo-4-Vinyl-2,3-diazabicyclo[3.3.0]oct-2-ene 1[2], which were, as well as the earlier reported decomposition reactions of 3-Vinyl-1-pyrazoline 2[3], interpreted in terms of allylic 1.3-diradicals as intermediates (eq 1).



(1)

We wish to report now data on the photochemical and thermal decomposition of the cis- and trans-3,5-divinyl-1-pyrazolines 3a,b and exo-4-vinyl-2,3-diazabicyclo[3.3.0]octa-2,7-diene 4. These systems allow for the first time decomposition studies which could be interpreted in terms of diallylic 1.3-diradicals.



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3a and 3b were synthesized by 1.3-dipolar cycloaddition of 3-diazopropene 5 to 1,3-butadiene (I, eq 2)[4]. An etheral solution of 5 with a tenfold excess of 1,3-butadiene was kept at +4°C for 4 days (discharge of red color). After removal of excess 1,3-butadiene and solvent at -10°C in a closed vacuum system the residue was purified by chromatography on Florisil (0°C, CH_2Cl_2, N_2), followed by trap-trap or normal distillation ($Kp_3 > 38^oC$,fast decomposition) to yield 45%(based on 5) of a mixture of 3a and 3b.At the indicated reaction temperature the competing intramolecular cyclysation of 5 to pyrazole 6 ($k_{25^oC}=2.3 \times 10^{-4}\ sec^{-1}$)[5] is minimized and allows reasonable yields of the 1.3-dipolar cycloadducts[6].

3a:^{1}H-NMR(CCl_4):δ=1.58(t,H_1,H_2;$J_{H_1-H_3}$ =7.0 Hz),4.30-5.15(m,H_3,H_4),5.15-5.60 (m,H_a,H_b),5.60-6.35(m,H_c)ppm;3b:^{1}H-NMR(CCl_4):δ=1.10(m,H_1;$J_{H_1-H_2}$ =12.5Hz,$J_{H_2-H_3}$= 9.5Hz),2.15(m,H_2;$J_{H_2-H_4}$ =8.0Hz),4.30-5.15(m,H_3,H_4),5.15-5.60(m,H_a,H_b),5.60-6.35 (m,H_c)ppm;from the NMR integration we can determine the ratio of 3b:3a =45:55 (compare fig.1 for the NMR data);for 3a + 3b:IR(Film):-(NH),3085,1635,1545(N=N), 983,920 cm^{-1};UV(hexane):$\lambda_{max}(\varepsilon)$=334 nm (240);MS(20eV): m/e=94(M^+-N_2),77,66.

The photodecomposition in solution and the gasphase thermolysis of 3a,b at 40-100°C are producing a mixture of trans-1,2-divinylcyclopropane 8 and 1,4-cycloheptadiene 10 (eq 3),whose proportions are listed in Table I[7].

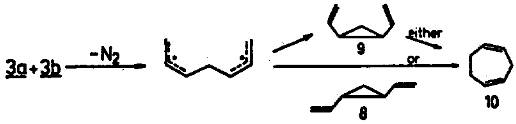

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Table I.Proportions of 8 and 10 in the decomposition of 3a and 3b[a].

REACTION CONDITIONS	% 8[b]	% 10[b]	P[d]
PHOTOLYSIS[c]	48.5	49.2	2.3
THERMOLYSIS(45,75,100°C)	38.1,36.6,32.4	61.5,63.0,67.0	0.4-0.6

a.All products were identified spectroscopically;b.average data from several runs c.pentane,pyrexfilter,Hanau TQ 180,0°C;d.tentatively from UV data assigned to be 1,3,5-heptatriene,pending further studies.

Whereas 8 is stable under the applied reaction conditions,10 is either derived from cis-1,2-divinylcyclopropane 9,which reportedly rearranges already at low temperatures into 10 or in part directly from a 1.3-diradical which could close to form 8 and 10 [8,9] (eq 3).Most strikingly the thermal decomposition of 3a and 3b starts already just above room temperature in measurable rates as demonstrated in Figure 1,where the decomposition of a solution of 3a and 3b in the probe of a Varian A60 NMR spectrometer is easily followed.

These observations can be interpreted in terms of formation of highly resonance stabilised diallylic 1.3-diradicals.Comparison of the decomposition tempe-

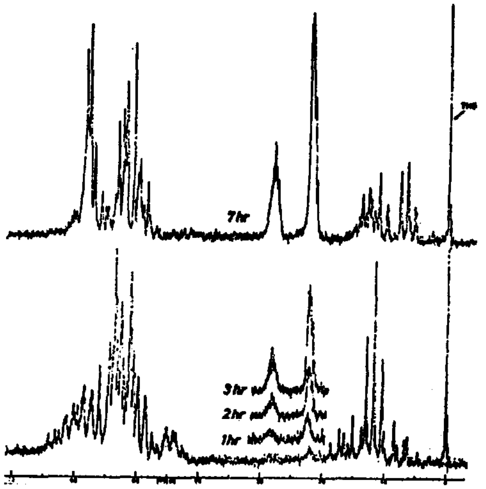

Fig.1. ^{1}H-NMR spectrum of a solution of 3a and 3b in C_6D_6 at probe temperature of a Varian A60 NMR spectrometer.The bottom spectrum shows the starting mixture and the top after 7 h a spectrum which is identical with the one of a mixture of 8 and 10.

ratures of 1-pyrazoline[10],1 and 2[2,3] and 3a and 3b show a decrease in this order from 220°C → 120°C → 30°C for a measurable first order rate.So it seems that the successive introduction of vinylgroups at the α-C of the C-N-bonds in 1-pyrazoline decreases the decomposition temperature by roughly 100°C per vinyl group.The formation of a diallylic 1.3-diradical seems therefore very likely.

In an independent investigation Crawford et al are studying the kinetics of the decomposition of 3a and 3b in solution and find from their data strong indications for the contribution of both vinyl groups to the decrease of activation enthalpy and therefore to the concertedness of the cleavage of both C-N-bonds[11].

Since it proved to be impossible to separate 3a and 3b to study them separately,we synthesized,in order to obtain a pure trans-3,5-divinyl system,compound 4 by 1.3-dipolar addition of 5 to cyclopentadiene (II,eq 2).A solution of 5,prepared in cyclopentadiene was kept for 5 days at +4°C until the red color had discharged.Competing side reactions are the formation of 6 and the fast addition of 5 to "dicyclopentadiene",which is formed during the reaction to yield 7[12]. Both reactions are causing the low yield of the cycloadduct[6].Distillation,repeated chromatography on Florisil(0°C,CH_2Cl_2,N_2) yields 5% (based on 5) of 4(Kp$_4$=48-50°C under decomposition).^{1}H-NMR(CCl_4):δ=1.70-2.20(m,3H),4.40-4.80(m,H_3),5.05-6.40(m,6H);the stereochemistry of the vinyl group was determined via the coupling constant of H_3 with the bridgehead proton in the analogous methyl compound[13]. IR(film):-(NH),3080,1640,1548(N=N),928,700 cm^{-1};UV(hexane):$\lambda_{max}(\epsilon)$=333 nm (265);

MS(11eV):m/e=134(M^+,8%),106(M^+-N_2),91,78,66,65,51.The thermal and photochemical decomposition of 4 produces exo- (11) and endo-6-vinylbicyclo[3.1.0]hex-2-ene 12 and bicyclo[3.2.1]octa-2,6-diene 13 (eq 4),whose proportions are listed in Table II[7].

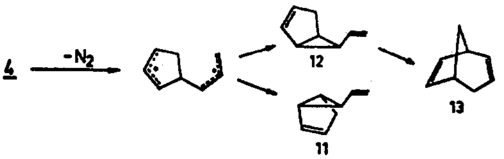

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Table II.Proportions of 11,12 and 13 in the decomposition of 4[a].

REACTION CONDITIONS	% 11[b]	% 12[b]	% 13[b]	P[d]
PHOTOLYSIS[c](0°C,RT)	68.5,69.5	4.4,0.0	27.2,30.5	trace
THERMOLYSIS (55,75,100°C)	60.0,56.5,48.5	22.5,4.5,0.0	17.6,39.0,51.5	-

a.All products were clearly identified spectroscopically;b.average data from several runs,thermolysis data obtained after reaction times of 5,10,15 min. well prior to completion,photolysis data after concentrating samples;c.pentane,pyrex filter,Hanau TQ180;d.compare ref.7

Whereas 11 is stable under the applied conditions,12 is converting into 13,the amount depending on the reaction temperature ($t_{1/2}^{25^oC}$ =1 d,$t_{1/2}^{40^oC}$= 25 min. $t_{1/2}^{53^oC}$ = 6 min.)[14].12 can therefore be observed at the lower decomposition temperatures(see Table II),provided the reaction is broken up well prior to completion and the analysis is carried out immediately.4 is decomposing in measurable rates around 20°C higher than 3a,b and we are currently studying the kinetics of 4 in solution in order to compare the data with those of 3a.Above systems seem to be well suited for the study of diallylic 1.3-diradicals and we are investigating their reactions currently in greater detail.

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