Tetrahedron. Vol 32, pp. 619 to 621. Pergamon Press 1976. Printed in Great Britain

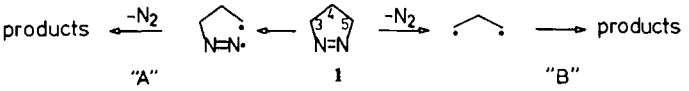
THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF *CIS*- AND *TRANS*-3,5-DIPHENYL-1-PYRAZOLINE

M. SCHNEIDER* and H. STROHÄCKER
Institut für Chemie, University of Hohenheim, Stuttgart, Germany

(*Received in the UK 2 October* 1975; *Accepted for publication 20 October* 1975)

Abstract—The decomposition mechanism of the title compounds **8c** and **8t** is discussed. Dibenzylic 1,3-biradicals are suggested as intermediates.

1-pyrazolines undergo thermal and photochemical decomposition presumably via the intermediacy of biradicals, whose detailed structure is still a matter of discussion. If both C–N-bonds in **1** are broken simultaneously (**B**), we obtain a nitrogen free intermediate, whereas the cleavage of only one bond would lead to products via the formation of diazenyl biradicals (**A**).



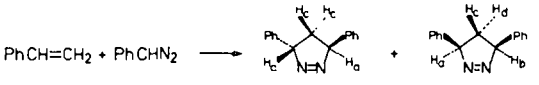
"A" **1** "B"

Kinetic data have been extensively used to distinguish between possible mechanisms. The influence of alkyl substituents in the 3- and 5-positions of **1** on the activation enthalpy of decomposition is very small, thus reducing the value of kinetic information in these systems. From stereochemical studies it is very likely that they decompose via pathway **A**. Kinetic data have been useful with vinyl substituted 1-pyrazolines where the contribution towards the lowering of the activation enthalpy by the vinyl group amounts to 8–10 kcal/mole. This is close to the accepted delocalisation energy (rotational barrier) of an allylic radical.

The decomposition reactions[1–4] of the *cis*- and *trans* - 3,5 - divinyl - 1 - pyrazolines (**2c** and **2t**) are the first examples for a concerted cleavage of both C–N-bonds, involving a highly stabilised diallylic biradical (**3**) with high rotational barrier and considerable life time.†

One would expect, that systems capable of producing dibenzylic 1,3-biradicals would behave similarly, since the contribution by a phenyl group towards the lowering of the activation enthalpy is in the order of 6–7 kcal/mole.[6] Earlier workers reported *trans*-3,5-diphenyl-1-pyrazoline (**8t**) to be the only product from the 1,3-dipolar cycloaddition of phenyldiazomethane to styrene.[7] Since there is no plausible reason for the formation of only one isomer in this reaction and *cis* - 3,5 - diphenyl - 1 - pyrazoline (**8c**) is essential for the study of the stereochemistry of the decomposition reactions, we decided to examine the system in detail.

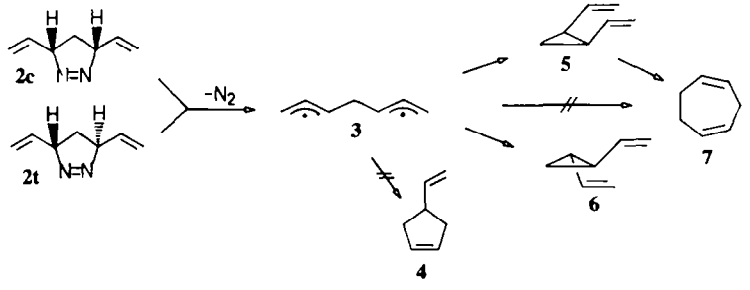
As expected, the 1,3-dipolar cycloaddition (for modified conditions, see Experimental) produces a 60:40 mixture of **8t**:**8c** in practically quantitative yield.



8t **8c**

Compounds **8c** and **8t** can be separated by fractional crystallisation, followed by column chromatography. The extreme difference in solubility between **8c** and **8t** and the thermolability of **8c** probably prevented its earlier detection. Both **8c** and **8t** are air sensitive and are readily tautomerised to the 2-pyrazoline by traces of acid or base. All handling and purifications were carried out at room temp. under N_2. All solvents used were carefully degassed.

The NMR of **8t** consists of two triplets at $\delta = 2{\cdot}13$ ($2H_a$) and 5·83 ($2H_c$) with the aromatic protons at 7·28 ppm. In the NMR of **8c** the non equivalence of H_a and H_b causes the splitting with two sets of protons centered at $\delta = 2{\cdot}07$ ($H_{c,d}$) and 5·28 ($H_{a,b}$), the aromatic protons being at

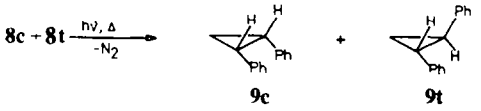


†2c and 2t produce only **5** and **6** in equal amounts, suggesting a common intermediate. No **4** and **7** is observed, whose formation would require rotations in **3** causing the loss of resonance energy of 12–14 kcal/mole and allylic bond.[5]

7·49 ppm. The coupling constants $J_{a,c} = 10·9$ Hz and $J_{a,d} = 8$ Hz in the NMR of **8c** suggest a puckering of the pyrazoline ring of *ca* 30° out of plane in agreement with models indicating this as conformation of choice to accommodate the phenyl groups. Compound **8t** is almost planar ($J_{a,c} = 7·8$ Hz), the ring puckering being less than 15°, also in agreement with model considerations.

The only thermal and photochemical decomposition products of **8c** and **8t** are *cis*- and *trans*-1,2-diphenylcyclopropanes (**9c** and **9t**) the proportions being listed in Table 1.

These proportions are somewhat dependent on the temperature between 45° and 150° (Table 2). At 45°, **8t** produces 8% **9c** and 92% **9t**, the ratio changing gradually to 13% **9c** and 87% **9t** at 150°. A smaller effect is observed in **8c**, the amount of **9c** increasing from 44% at 45° to 47% at 150° while the amount of **9t** decreases proportionately. In all cases, especially the slower runs, it was carefully checked that all **8c** and **8t** was completely decomposed prior to analysis. Interconversion of **9c** and **9t** is negligible under the conditions used. If it did occur, more of the thermodynamically more stable **9t** would be produced at higher temperatures. This is in contrast to the observations.



9c **9t**

Table 1. Decomposition products of **8c** and **8t**

	Yield (%)			
	Thermal 40–80°C[a]		Photochemical	
	9c	**9t**	**9c**	**9t**
8c	45	55	51·5	48·5
8t	11	89	14·5	85·5

[a]data are temperature dependent, see Table 2.

Table 2. Temperature dependence in the thermolysis of **8c** and **8t**

	Yield (%)			
	8c		**8t**	
T(°C)	**9c**	**9t**	**9c**	**9t**
45	44	56	8	92
60	45	55	9·5	90·5
80	45·5	54·5	10	90
100	46·5	53·5	11	89
120	47·5	52·5	11·5	88·5
150	47·5	52·5	12·5	87·5

The value originally reported for the activation energy in the decomposition of **8t** was 11·6 kcal/mole. It has been corrected[6] to 27·5 kcal/mole, and is identical with our check experiments. The activation parameters† of **8c** ($\Delta H^{\dagger} = 25·0 \pm 1$ kcal/mole; $\Delta S^{\dagger} = 0 \pm 3$ cal . K^{-1} . mole^{-1}) show that it decomposes much faster than the *trans*-compound. From the kinetic data it seems that both phenyl substituents are contributing‡ (up to 8 kcal/mole per phenyl group) towards the decrease of activation enthalpy, suggesting the formation of stabilised dibenzylic 1,3-biradicals via simultaneous cleavage of both C–N-bonds.

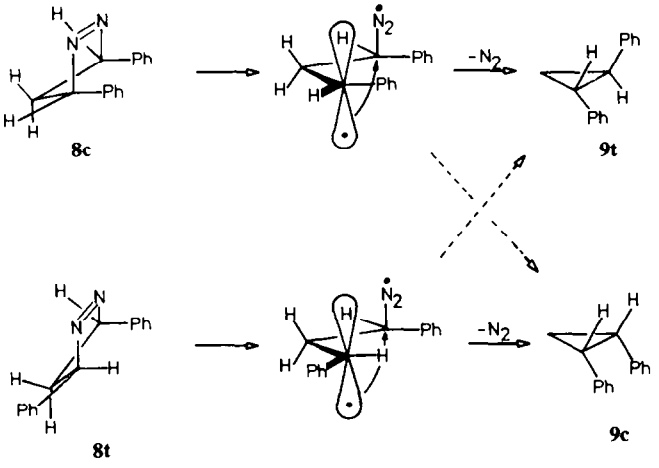
The product proportions observed are quite different from those for 3,5 - *dialkyl* - 1 - pyrazolines,[8] which yield different proportions in the photochemical and thermal reactions. The observed *inversion* in the thermal process could be attributed to a "two-step" mechanism. If we apply this scheme in the decomposition of **8c** and **8t**, then we would expect **8c** to produce mainly **9t** and **8t** would yield larger amounts of **9c** (Scheme 1).

This is definitely not the case and all earlier claims of a stereospecific decomposition of **8t** are unjustified.[7]

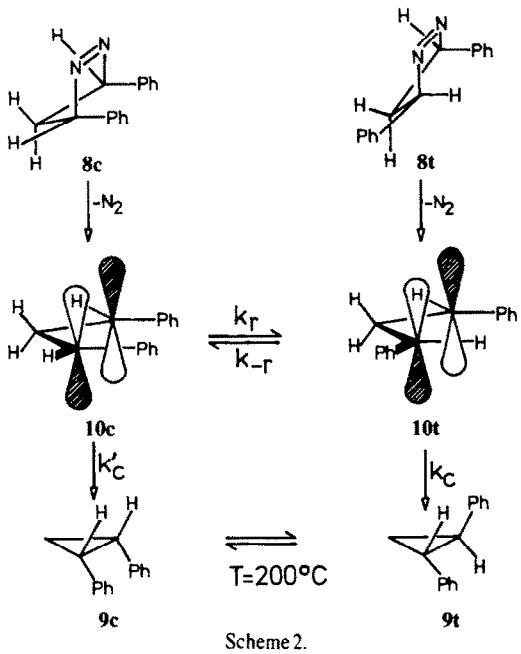
The product proportions together with the kinetic information are in agreement with Scheme 2. The decomposition of **8c** and **8t** produces primarily the two isomeric biradicals by simultaneous cleavage of both C–N-bonds. The product proportions are a result of the competition between ring closure (k_c and k'_c) and the rotational isomerism (k_r and k_{-r}) of the intermediate biradicals. A simple steady state treatment of the product data (neglecting back rotations of **10c** and **10t**) reveals that k_r/k_c (responsible for the formation of **9t**) is roughly 5 times larger than k_{-r}/k'_c (which is leading to **9c**). The observed temperature dependence (producing more thermodynamically less stable **9c** at higher temperatures) suggests, that at higher temperatures the rotational

†The data are preliminary, a detailed study of a series of 1-pyrazolines is in progress.

‡In reference to **1** ($\Delta H^{\ddagger} = 41$ kcal/mole).



Scheme 1.



Scheme 2.

isomerism is competing favorably with the ring closure reaction.

The same type of intermediate is probably involved in the interconversion of **9c** and **9t** above 200°. This reaction, starting from both **9c** and **9t** yields an identical thermodynamic equilibrium mixture (K = 10). 3,5-Divinyl- and diphenyl-1-pyrazolines therefore decompose via simultaneous cleavage of both C–N bonds, yielding highly stabilised diallylic and dibenzylic 1,3-biradicals as intermediates.

EXPERIMENTAL

M.ps are uncorrected. NMR spectra were taken on Varian EM 360, A60A and Bruker XF 90; IR spectra in CCl_4 on Perkin Elmer 457 and 221; UV spectra on a Zeiss DMR 10; Mass spectra on a Varian MAT 711. Elementary analysis were carried out in the Microanalytical Laboratory of the University of Stuttgart. VPC analysis: Varian 1200 on 6′ × 1/8″ SE 30 column on Chromosorb W-AW-DMCS at 140°.

cis- *and* trans - 3,5 - *Diphenyl* - 1 - *pyrazolines* (**8c** *and* **8t**). Phenyldiazomethane was prepared by the usual procedure via oxidation of benzaldehydrazone with mercuric oxide.[7] In contrast to earlier preparations, the phenyldiazomethane was carefully (!!) distilled under vacuum immediately prior to use. In a typical preparation 6·4 g (54 mmoles) of phenyldiazomethane were dissolved in 50 ml n-pentane at 0°. To this mixture 5·8 g (56 mmoles) of freshly distilled styrene were added, and the mixture was kept at +4° until the deep red colour of the mixture had completely discharged (3–4 days). During the reaction large amounts of crystalline **8t** precipitated and were removed. The final solution obtained was further concentrated at 0° and successive crops of **8t** were isolated. From the final mother liquor obtained, **8c** was isolated by evaporation of the soln almost to dryness. The total amount of material recovered was 12·0 g corresponding to a 96% yield (based on phenyldiazomethane). Both compounds could be further purified by column chromatography on *Florisil*, using CH_2Cl_2 as eluant.

After final purification, **8c** (3·6 g; 16 mmoles) was isolated from the mixture (30% over all yield based on phenyldiazomethane) as white crystals, m.p. 53–55° (dec); IR: 1535 cm^{-1} (N=N); NMR $\delta_{ppm}^{CDCl_3}$: 1·39 (H_c, $J_{a,c}$ = 10·9, $J_{c,d}$ = 12·9 Hz), 2·75 (H_d, $J_{a,d}$ = 8·0 Hz), 5·28 ($H_{a,b}$, q), 7·49 (10 H_{arom}, s); UV: 323 nm (350); MS (70 eV): *m/e* = 222·1 (M^+, 40%), 194·1 (M^+-N_2, base peak, 100%). (Found: C, 80·88; H, 6·40; N, 12·48. Calc. for $C_{15}H_{14}N_2$: C, 81·05; H, 6·35; N, 12·60%).

After final purification, **8t** (6·8 g; 31 mmoles) was isolated from the mixture (57% over all yield based on phenyldiazomethane) as white crystals, m.p. 109–110° (fast dec prior to melting). Satisfactory analytical data were only obtained after chromatography on Florisil. We could not obtain pure products by recrystallisation from MeOH. IR: 1542 cm^{-1} (N=N); NMR $\delta_{ppm}^{CDCl_3}$: 2·13 ($2H_c$, t, J = 7·8 Hz), 5·83 ($H_{a,b}$, t), 7·28 ($10H_{arom}$, m); UV: 326 (413); MS (70 eV): *m/e* = 222 (M^+, 35%), 194 (M^+-N_2, base peak, 100%). (Found: C, 80·78; H, 6·35; N, 12·96. Calc. for $C_{15}H_{14}N_2$: C, 81·05; H, 6·35; N, 12·60%).

cis - 1,2 - *Diphenylcyclopropane* (**9c**) *and* trans - 1,2 - *diphenylcyclopropane* (**9t**). Reaction products from the thermolysis and photolysis of **8c** and **8t** were identical with authentic samples.[9]

Thermal decompositions. 2–5 mg portions of **8c** and **8t** were dissolved in benzene and sealed, after degassing under vacuum, in pyrex tubes. The tubes were thermolised in a thermostated silicon oil bath and analysed by VPC. The complete decomposition was monitored by UV and NMR in parallel samples. All reactions were carried out with neat samples.

Photochemical decompositions. 1% solns of **8c** and **8t** dissolved in 3-methylbutane were irradiated, after degassing at −5°, with a Hanau TQ 150 high pressure mercury lamp (pyrex filter) in a Normag photochemical reactor. The decomposition was monitored by UV. Irradiations were also carried out directly at −50° in $CDCl_3$ in NMR tubes with a lens-dewar assembly (Phillips HPK 125 lamp and Schott UG1 filter) or in the cavity of the NMR spectrometer. All samples were analysed by NMR and checked by VPC.

Temperature dependence studies. 5 mg samples of **8c** and **8t** were sealed under vacuum in pyrex tubes and thermolised at temps between 45° and 150° (cf Table 2). All decompositions were monitored carefully and extended to more than 10 half lifes. This is especially important in the low temp runs, since partial decomposition will cause incorrect results because the samples are then decomposed in the hot injection port of the VPC.

Kinetic measurements. The decomposition reactions were followed manometrically in an apparatus already described[10] by measuring the evolved N_2. The reaction cell was immersed in a thermostated bath and all reactions were monitored to more than 10 half lifes to determine infinite volumes.

Acknowledgements—We thank Prof. Dr W. Kraus for his interest in this research. This work was supported by the "Deutsche Forschungsgemeinschaft".

LITERATURE

[1]R. J. Crawford and M. Ohno, *Canad. J. Chem.* **52**, 3134 (1974).
[2]M. Schneider and G. Mössinger, *Tetrahedron Letters.* 3081 (1974).
[3]M. Schneider and J. Rebell, *J. Chem. Soc. Chem. Commun.* 283 (1975).
[4]M. Schneider, *Angew. Chem.* **87**, 717 (1975); Angew. Chem. intermat. Edit. **14**, 707 (1975).
[5]W. v. E. Doering and G. H. Beasley, *Tetrahedron* **29**, 2231 (1973); W. R. Roth, G. Ruf and P. W. Ford, *Chem. Ber.* **107**, 48 (1974).
[6]J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.* **92**, 978 (1970); J. W. Timberlake and B. K. Bandlish, *Tetrahedron Letters* 1393 (1971).
[7]C. G. Overberger and J. P. Anselme, *J. Am. Chem. Soc.* **84**, 869 (1962); C. G. Overberger, J. P. Anselme and J. R. Hall, *Ibid.* **85**, 2752 (1963); C. G. Overberger and J. P. Anselme, *Ibid.* **86**, 658 (1964); C. G. Overberger, N. Weinshenker and J. P. Anselme, *Ibid.* **86**, 5364 (1964); C. G. Overberger, N. Weinshenker and J. P. Anselme, *Ibid.* **87**, 4119 (1965).
[8]R. J. Crawford and A. Mishra, *Ibid.* **88**, 3963 (1966); R. Moore, A. Mishra and R. J. Crawford, *Canad. J. Chem.* **46**, 3305 (1968).
[9]S. G. Beech, J. H. Turnbull and W. Wilson, *J. Chem. Soc.* 4686 (1952); D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Am. Chem. Soc.* **83**, 4838 (1961).
[10]R. C. Peterson, J. M. Markgraf and S. D. Ross, *Ibid.* **83**, 3819 (1961); J. P. Deleux, G. Leroy and L. Weiler, *Tetrahedron* **29**, 1135 (1973).