Photolysis of *cis*- and *trans*-3,5-Diphenyl-1-pyrazolines: Competing Trimethylene and Cycloreversion Pathways

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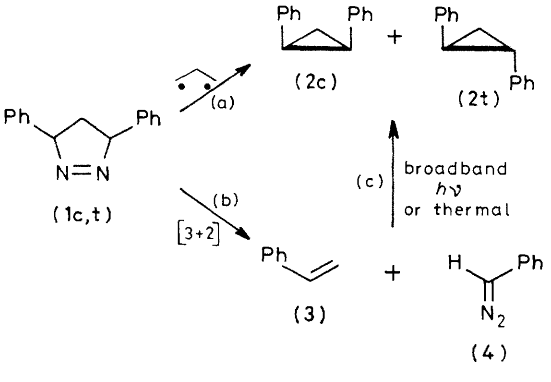
Summary In the photolysis of the title compounds up to 30% of the reactions are proceeding *via* cycloreversions producing styrene and phenyldiazomethane.

Decompositions of 1-pyrazolines have frequently been interpreted in terms of various trimethylene intermediates[1] [(a) Scheme]. [3 + 2] Cycloreversions, yielding olefins and diazocompounds [(b) Scheme], can, in principle, compete effectively with these processes and cycloreversion products have been characterised for 1-pyrazolines with a bicyclo-[3.1.0] framework.[2] Cycloreversion products have also been suggested, on the basis of product studies,[3] e.s.r. spectroscopy, and trapping experiments,[4] to be involved in the decomposition of simple monocyclic 1-pyrazolines, but no definite or quantitative evidence for these primary products has been given. To differentiate between these processes and thus to provide a concise mechanistic interpretation a quantitative determination of all primary products is crucial. This is especially important in cases, *e.g.* with the title compounds, where both pathways may ultimately lead to identical reaction products [(c) Scheme].[5]



Scheme

Degassed 10^{-3} molar solutions of *cis*- or *trans*-3,5-diphenyl-1-pyrazoline (**1c**) or (**1t**) in a number of solvents (Table) were irradiated at −20 °C [+ 4 °C for benzene; (**1c**) is stable only at low temperature] with monochromatic (330 ± 10 nm, Osram XBO 1600 W Xenon lamp with monochromator) u.v. light. The reactions were monitored by the decay of the $n \rightarrow \pi^*$ transitions of (**1c**) and (**1t**) at 330 and 332 nm, respectively. After completion, the resulting solutions containing *cis*- and *trans*-1,2-diphenylcyclopropane (**2c**) and (**2t**), styrene (**3**), and phenyldiazomethane (**4**) were treated with a slight excess of HOAc [(**4**)→benzyl acetate] and analysed by H.P.L.C. and V.P.C. The results are presented in the Table.

Alternatively, a spectroscopic low conversion (⩽30%) study of the photolysis of (**1t**) at room temperature allows a direct and quantitative determination of (**1t**) at 330 nm and (**4**) (which in high concentration is actually visible as a red colour) at 308 nm, their absorption coefficients being

TABLE Properties of biradical and cycloreversion products (mol %) in the photolysis of (**1c**) and (**1t**) from chromatographic and spectroscopic analysis[c]

Compound	Solvent	Biradical[a] (**2c**)	Biradical[a] (**2t**)	Cycloreversion[a] (**3**)	Cycloreversion[b] (**4**)
(**1c**)	Acetonitrile	55	40	4	
(**1t**)		7	75	8	12
(**1c**)	EtOH	50	40	5	
(**1t**)		6·5	80	10	10
(**1c**)	Benzene	52	35	13	
(**1t**)		6	80	13	22
(**1c**)	n-Hexane	40	33	17	
(**1t**)		6	63	23	30

[a] Chromatographic analysis [b] Spectroscopic analysis [c] Some decomposition of (**4**) cannot be excluded completely, leading to different results from the chromatographic and spectroscopic analyses

known The proportions of (**4**), formed in the early stages of the reaction, are given in the Table Careful spectroscopic and chromatographic studies at various stages of the reaction revealed that the amount of (**3**) and (**4**) passes through a maximum, and decreases again with continued irradiation This is the reason for the higher values obtained spectroscopically

The data indicate that cycloreversions (avoiding biradical intermediates) are responsible for up to 30% of the decomposition reactions of (**1c**) and (**1t**), an amount which has certainly been underestimated in the past This may be due to the fact that broadband irradiation has usually been employed On the basis of the present work, therefore, the direct fragmentation into carbenes, previously discussed[3b] seems rather unlikely

The results suggest that for a number of 1-pyrazolines cycloreversions and trimethylene processes may have rather similar energy requirements and that mechanistic interpretation must be based on a careful and quantitative evaluation of all possible reaction pathways

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[1] For a critical review see R G Bergman in 'Free Radicals,' Vol 1, ed J K Kochi, Wiley-Interscience, New York, 1973, pp 191—237

[2] By ^{1}H n m r spectroscopy M Schneider and B Csacsko, *Angew Chem , Int Ed Engl* , 1977, **16**, 867 and references cited therein

[3] (a) R Moore, A Mishra and R J Crawford, *Can J Chem* , 1968, **46**, 3305, (b) K L Rinehart and T V van Auken, *J Am Chem Soc* , 1960, **82**, 5251 1962 **84**, 3736

[4] S L Buchwalter and G L Closs, *J Org Chem* , 1975, **40**, 2549, G Ege, K Gilbert, and B Hahn, *Tetrahedron Lett* , 1979, 1571

[5] *Cf* earlier work with (**1t**) J W Timberlake and B K Bandlish, *Tetrahedron Lett* , 1971, 1395, (**1c**) and (**1t**) M Schneider and H. Strohacker, *Tetrahedron*, 1976, **32**, 619