Photochemical and Thermal Decomposition of 1-Pyrazolines

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Quantum yields for photochemical nitrogen extrusion from seven 1-pyrazolines were found to range from 0.12 to 0.88 but 4-oxo-3,3,5,5-tetramethyl-1-pyrazoline (**8**) proved to be photochemically and thermally remarkably stable. 4-Isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline (**7**) decomposed thermally with $E_a = 39.8$ kcal mol^{-1} and $\Delta S^{\neq} = 0.7$ e.u. The high stability of this compound contrasts with 4-methylene-1-pyrazoline (**17**).

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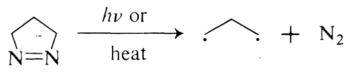
Les rendements quantiques de la formation d'azote par décomposition photochimique de sept pyrazolines-1 s'échelonnent de 0.12 à 0.88 mais l'oxo-4 tétraméthyl-3,3,5,5 pyrazoline-1 (**8**) est remarquablement stable du point de vue photochimique et thermique. Pour la décomposition thermique de l'isopropylidène-4 tétraméthyl-3,3,5,5 pyrazoline-1 (**7**), on a $E_a = 39.8$ kcal mol^{-1} et $\Delta S^{\neq} = 0.7$ e.u. La grande stabilité de ce composé est en contraste par rapport à celle du méthylène-4 pyrazoline-1 (**17**). [Traduit par le journal]

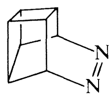
1-Pyrazolines have been studied intensively during the past several years with particular emphasis on the mechanism of their thermolysis (1) and photolysis (2), and on the fate of the resulting 1,3-biradical (3). These compounds are useful in the synthesis of cyclopropanes (4) whereas the closely related 4-alkylidene-1-pyrazolines (5) are important precursors to trimethylenemethane biradicals (6).



Since it is known that the photostability of azoalkanes varies widely (7), a study of the effect of structure on the efficiency of pyrazoline decomposition was considered to be of interest. We have found that direct photolysis of 1-pyrazolines in solution generally proceeds with high quantum yield. Additionally, remarkably high thermal stability has been noted for a 4-alkylidene-1-pyrazoline.

Most of the compounds employed in this study were prepared by standard synthetic methods; thus, **2** and **6** were made by cycloaddition (3*a*) of a diazoalkane (4*c*,*e*) to an olefinic ester, **3** and **4** by oxidative addition to 3,5,5-trimethyl-2-pyrazoline (8, 9), and **8** by oxidative cyclization of the diaminoketone (10). Compound **5** was obtained from **2** by lithium aluminum hydride reduction (11) whereas **7** was made from **8** by treatment with isopropyllithium followed by dehydration (10).

The quantum yields for nitrogen evolution shown in Table 1 were obtained using the photolysis of 2,3-diazabicyclo[2.2.1]heptene-2 (DBH) as an actinometer. The data show that photolysis of 1-pyrazolines is an efficient process, approaching in some cases the unit quantum yield of DBH. This may be taken as a good omen for the general success of cyclopropane synthesis from 1-pyrazolines, in contrast to the less cooperative 2,3-diazabicyclo[2.2.2]octene-2 systems **10**–**13** (refs. 13, 14, 7, and 15, respectively). The only exceptions in Table 1 are 3-chloropyrazoline **4** and the 4-ketopyrazoline **8**.



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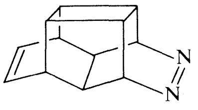

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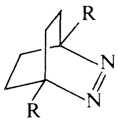

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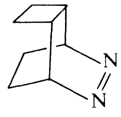
R = H, CH$_3$



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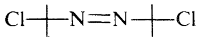
Compound **4** resembles the acyclic azoalkane **14**, which we have found to produce nitrogen



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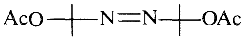

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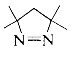
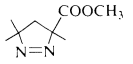
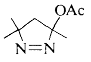
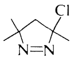
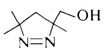
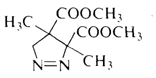
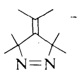
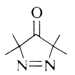
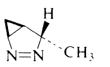
TABLE 1. Nitrogen quantum yields for 1-pyrazolines irradiated in benzene at 313 nm

Compound	Φ
 1	0.88
 2	0.86
 3	0.44
 4	0.12
 5	0.50
 6	0.52*
 7	0.45
 8	0.012
 9	0.86†

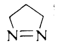
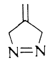
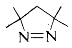
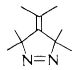
*Reference 16.
†Reference 12.

with a quantum yield of only 0.01 (16). Levi and Malament (17) have recently discovered that this apparent inertness is due to facile, reversible conversion of such compounds to an unstable intermediate in which the α-carbon has lost its stereochemistry (probably an *N*-chlorohydrazone). This reaction may account for the lower nitrogen quantum yield in **4**. Diacetoxy azoalkane **15** undergoes reversible photodissociation into an acetate anion and an α-azo carbonium ion (17) at the expense of nitrogen extrusion ($\Phi_{N_2} = 0.005$) (16) but the related pyrazoline **3** still produces nitrogen with good efficiency. We tentatively suggest that the photoepimerization reactions have geometric requirements which are not entirely met in pyrazolines. An alternate but unsatisfactory explanation recognizes that the primary photochemical act in most acyclic azoalkanes is isomerization to the labile *cis* form rather than nitrogen extrusion. The quantum yield data are therefore consistent with the following order of reaction rates: pyrazoline nitrogen extrusion > photoepimerization > *trans–cis* isomerization. The problem here is that the first reaction is not faster than the third, as evidenced by the observation of fluorescence in pyrazolines but not in acyclic azoalkanes, even *cis* ones.

Pyrazoline **8**, which possesses a 4-keto group, decomposes very inefficiently. Interestingly, the reluctance of this material to lose nitrogen was responsible for the failure of Mock's otherwise elegant synthesis of tetramethylcyclopropanone (10). Although reversible photoionization is not an attractive explanation in this case, the actual reason for the photostability of **8** is still unknown. An interaction between the two functional groups is seen in the photoelectron spectrum (18) of **8** but it is not apparent how this leads to rapid radiationless decay. Looking into the photochemistry of **8** a bit further, we found that the gas produced consisted of a 3:1 ratio of carbon monoxide and nitrogen.

During the course of this study, an attempt was made to effect thermal decomposition of **7** and **8**. To our surprise, both compounds were very stable. Thus, heating **8** for 4.5 h at 205° gave only about 35% decomposition. A more detailed study of **7** gave the activation parameters shown in Table 2, along with those for three other pyrazolines. Since the activation energy for thermolysis of **17** is about 10 kcal mol^{-1} lower than that for **16**, one might expect the same trend in **1** *vs.* **7**. Instead, the addition of an isopropylidene group to **1** raises the activation energy by 2 kcal mol^{-1}. The resonance stabilization inherent in the trimethylenemethane moiety must be manifested in the transition state for thermolysis of **17** but not of **7**. This would be the case if loss of nitrogen required considerable bending of the C—N bonds into the plane of the olefin π bond. Whereas such a motion encounters little hin-

TABLE 2. Activation parameters for thermolysis of 1-pyrazolines

Compound	E_a (kcal mol^{-1})	$\Delta S_{200}^{\ddagger}$ (e.u.)	k_{rel} (200°)	Reference
 16	42.4 ± 0.3	11.5 ± 0.6	1.0	1*a*
 17	32.6 ± 0.3	-0.9 ± 0.5	68.4	5*d*, 20
 1	37.7 ± 0.4	4.9 ± 0.8	5.4	1*a*
 7	39.8 ± 0.6	0.7 ± 1.1	0.069	This work

drance in **17**, this process in **7** forces the *cis* 3 and 5 methyl groups into close proximity. The activation energy difference between **1** and **7** could be due to a difference in ground state ring strain, with **7** being more stable. Crawford *et al.* have made a more complete study of systems like **7** and have reached similar conclusions (19, 20).

Experimental

General

Ultraviolet spectra were run in hexane on a Cary 17 spectrophotometer. Nuclear magnetic resonance spectra were taken on a Varian A 56-60 in CCl_4 unless otherwise specified.

Synthesis

The published synthesis (21) of **1** was only minimally successful in our hands. The compound was purified by recrystallization from pentane at −78° followed by vacuum distillation, b.p. 74–75°/63 mm; u.v. λ_{max} 327 nm, ε 204. Pyrazoline **2** (11) was prepared in 63% yield from 2-diazopropane (4*c*) and methyl methacrylate, b.p. 69–71°/0.5 mm; u.v. λ_{max} 327 nm, ε 165. Lead tetraacetate oxidation (8) of 3,5,5-trimethyl-2-pyrazoline afforded compound **3** in moderate yield, b.p. 42.5°/0.1 mm; u.v. λ_{max} 330 nm, ε 214. Pyrazoline **4** was synthesized by an extension of the method used on phenylhydrazones (9). 3,5,5-Trimethyl-2-pyrazoline (4.6 g) (21) in 50 cc methylene chloride was cooled to −50° and chlorine gas was bubbled in. The initially cloudy solution became a clear, deep yellow within 15 min. After the solution had warmed to ambient temperature, the solvent was removed by rotary evaporation and the residue was distilled, b.p. 56°/10 mm; yield 4.2 g; u.v. λ_{max} 332 nm, ε 105; n.m.r. (deuteriobenzene): δ 1.10, 1.18, 1.67 (methyls), AB quartet centered at 1.44, $J = 14$ Hz (CH_2). Lithium aluminum hydride reduction of pyrazoline **2** followed by mercuric oxide oxidation gave **5** (11) in 47% overall yield, b.p. 74–75°/0.5 mm; u.v. λ_{max} 328 nm, ε 185; n.m.r. δ 1.26, 1.34, 1.40 (methyls), AB quartet centered at 1.37, $J = 12.5$ Hz (ring CH_2), AB quartet centered at 3.68, $J = 11.9$ Hz (CH_2). Compound **6** (λ_{max} 330 nm, ε 242) was a gift from S. R. Wilson while **7** (λ_{max} 324 nm, ε 162) and **8** (λ_{max} 356 nm, ε 164) were made without difficulty according to Mock's procedure (10).

Quantum Yields

0.05 *M* solutions of the pyrazolines were irradiated in a photochemical merry-go-round with 313 nm light isolated by an aqueous potassium chromate filter. Nitrogen yields were measured with a Töpler pump and gas buret and were compared with the gas yield from identical solutions of 2,3-diazacicyclo[2.2.1]heptene-2.

Kinetic Studies

Approximately 0.01 *M* solutions of pyrazoline **7** in hexadecane were degassed and sealed into 1 cm Pyrex u.v. cells. These were heated six at a time in a high temperature silicone oil bath. Tubes were removed periodically and their absorbance determined on the Cary 17. The rate constants, which were computed using a least squares treatment, were as follows: (temperature °C, $k \times 10^4\ \mathrm{s}^{-1}$) 218.88, 0.772; 227.98, 1.641; 234.75, 2.750. The activation parameters are shown in Table 2.

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1. (*a*) R. J. CRAWFORD and A. MISHRA. J. Am. Chem. Soc. **88**, 3963 (1966); (*b*) J. W. TIMBERLAKE and B. K. BANDLISH. Tetrahedron Lett. 1393 (1971).
2. (*a*) R. MOORE, A. MISHRA, and R. J. CRAWFORD. Can. J. Chem. **46**, 3305, (1968); (*b*) G. L. LOPER and F. H. DORER. J. Am. Chem. Soc. **95**, 20 (1973).
3. (*a*) D. MCGREER, N. W. K. CHIU, M. G. VINJE, and K. C. K. WONG. Can. J. Chem. **43**, 1407 (1965); (*b*) C. G. OVERBERGER, N. WEINSHENKER, and J. P. ANSELME. J. Am. Chem. Soc. **86**, 5364 (1964); (*c*) M. SCHNEIDER and R. J. CRAWFORD. Can. J.

Chem. **48**, 628 (1970); D. H. White, P. B. Condit, and R. G. Bergman. J. Am. Chem. Soc. **94**, 7931 (1972).

4. (*a*) D. C. Pittmer and R. Glassman. J. Org. Chem. **35**, 999 (1970); (*b*) E. L. Allred and J. C. Hinshaw. J. Am. Chem. Soc. **90**, 6885 (1968); (*c*) S. D. Andrews, A. C. Day, P. Raymond, and M. C. Whiting. Org. Synth. **50**, 27 (1970); (*d*) C. Berger, M. Franck-Neumann, and G. Ourisson. Tetrahedron Lett. 3451 (1968); (*e*) G. W. Cowell and A. Ledwith. Q. Rev. **24**, 119 (1970).
5. (*a*) P. Dowd. J. Am. Chem. Soc. **88**, 2587 (1966); (*b*) H. Kato. Chem. Commun. 496 (1968); (*c*) S. D. Andrews and A. C. Day. J. Chem. Soc. **B**, 1271 (1968); (*d*) R. J. Crawford and D. M. Cameron. J. Am. Chem. Soc. **88**, 2589 (1966); (*e*) J. J. Gajewski, A. Yeshurun, and E. S. Bair. J. Am. Chem. Soc. **94**, 2138 (1972).
6. P. Dowd. Acc. Chem. Res. **5**, 242 (1972).
7. P. S. Engel and C. Steel. Acc. Chem. Res. **6**, 275 (1973).
8. J. P. Freeman. J. Org. Chem. **28**, 885 (1963).
9. M. W. Moon. J. Org. Chem. **37**, 383 (1972).
10. W. L. Mock. Ph.D. Thesis, Harvard University, Cambridge, Mass. 1964.
11. E. L. Allred and C. R. Flynn. J. Am. Chem. Soc. **94**, 5891 (1972).
12. D. F. Eaton. Ph.D. Thesis, California Institute of Technology, Pasadena, California. 1972.
13. J. P. Snyder. Ph.D. Thesis, Cornell University, Ithaca, N.Y. 1965. Diss. Abstr. **26**, 5728 (1966); D. W. McNeil, M. E. Kent, E. Hedaya, P. F. D'Angelo, and P. O. Schissel. J. Am. Chem. Soc. **93**, 3817 (1971).
14. J. A. Berson and R. F. Davis. J. Am. Chem. Soc. **94**, 3658 (1972).
15. H. Tanida, S. Teratake, Y. Hata, and M. Watanabe. Tetrahedron Lett. 5341 (1969).
16. P. S. Engel and D. J. Bishop. Unpublished results.
17. N. Levi and D. S. Malament. Israel. J. Chem. In press.
18. K. N. Houk, Y. M. Chang, and P. S. Engel. J. Am. Chem. Soc. Submitted.
19. R. J. Crawford and H. Tokunaga. Can. J. Chem. This issue.
20. R. J. Crawford, D. M. Cameron, and T. Tokunaga. Can. J. Chem. This issue.
21. R. J. Crawford, A. Mishra, and R. J. Dummel. J. Am. Chem. Soc. **88**, 3959 (1966).