Pyrazolinone Carbonyl Ylides: Novel Photochemistry of Oxiran and Diazo-compounds[1]

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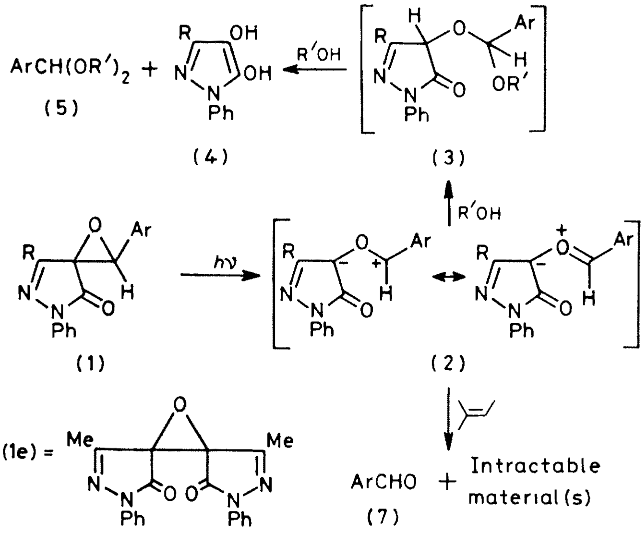
Summary A series of oxopyrazoline-4-spiro-oxirans and 4-diazo-3-methyl-1-phenyl-5-oxo-2-pyrazoline have been photolysed to generate reactive intermediates incorporating the pyrazolinone ring, which have been trapped with nucleophilic solvents and investigated by spectroscopic techniques.

Earlier efforts to rationalize the isolation of an oxopyrazoline-4-spiro-oxiran as the chief product of the photooxidation in acetone of an oxopyrazolidine[2] encouraged us to determine whether the oxopyrazoline-4-spiro-oxirans (**1**) might serve as precursors for novel oxopyrazoline carbenes On the basis of previous experience[3] we expected that the electrocyclic opening of the oxirans (**1**) would occur preferentially to give carbonyl ylides, the electronic character of which would be most accurately represented by the structures (**2**).† Thus we predicted that such systems as (**1**) would give the heterocyclic carbenes (**6**) in preference to aryl counterparts.

The novel class of oxopyrazoline-4-spiro-oxirans (**1**)‡ are easily made by basic peroxide oxidation[4] of the corresponding 4-arylidene oxopyrazolines.[5]‡ The colourless, symmetrical dioxopyrazoline spiro-oxiran-spiro-pyrazoline (**1e**)‡ is prepared by oxidation of the intensely blue 3,3′-dimethyl-1,1′-diphenyl-[$\Delta^{4,4'}$-bi-(2-pyrazoline)]-5,5′-dione[5a,6] and undergoes rapid deoxygenation back to it upon melting or in the presence of stilbene upon heating in toluene under reflux.



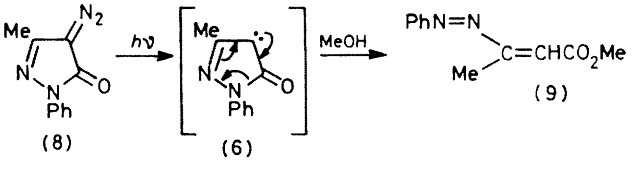
a, R = Me Ar = Ph
b, R = Me Ar = 2-naphthyl R′ = Me
c, R = Ph Ar = 2-naphthyl R′ = Me
d, R = Ph Ar = Ph

Irradiation§ at 254 nm of the spiro-oxirans (**1a**) and (**1b**) in a matrix of 3-methylpentane at −196 °C gives rise to intermediates with absorption spectra characteristic of carbonyl ylides.[3b,c] The transient species derived from (**1a**) and (**1b**) have absorption maxima at 505, 675 and 530, 728 nm, respectively. The latter transient is also observed during the nanosecond laser-flash photolysis[7] of (**1b**) in benzene at 22 °C, (λ_{max} 535 and 735 nm), decays with a lifetime (τ) of 1·6 ± 0·1 μs, and is efficiently quenched by methanol with a rate constant of $6{\cdot}0 \times 10^{8}$ l mol^{-1} s^{-1}. Laser photolysis of (**1e**), on the other hand, gives a transient with spectral maxima at 425 and about 725 nm (in benzene) and a decay lifetime of 0·52 ± 0·02 μs. No quenching of the transient by methanol is observed in this case and there is an increase in the lifetime on increasing solvent polarity, that is, τ = 0·60 ± 0·02 μs in acetonitrile and 0·74 ± 0·02 μs in benzene–methanol (1:1). The lifetimes and solvent behaviour of these intermediates are very similar to those of the ylides[8] derived from stilbene oxides and other oxirans at room temperature.

Attempts to intercept the carbonyl ylides (**2**) with electron-rich and electron-poor dipolarophiles such as 2,3-dimethylbut-2-ene and dimethyl maleate proved unrewarding. The carbonyl ylides (**2b**) and (**2c**), however, can be trapped by methanol or water. 4,5-Dihydroxy-3-methyl-1-phenylpyrazole (**4b**)[9] is formed when (**1b**) is irradiated at 350 nm in methanol, or in 0·6 M water or methanol in acetone, along with 2-naphthaldehyde [detected as its dimethyl acetal (**5b**) when methanol is present]. The acetal (**5c**) and 4,5-dihydroxy-1,3-diphenylpyrazole (**4c**)[10] are formed when the oxiran (**1c**) is irradiated in methanol. On the basis of earlier experience with carbonyl ylides in methanol[3e] we postulate that the ylides (**2b**) and (**2c**) react with water or methanol to give the acetals (**3**), which are subsequently converted into the dihydroxypyrazoles (**4**) and the aldehyde (**7b**) or its acetal (**5b**) respectively. These results confirm our contention that ylides are correctly represented as (**2**) form when the oxirans (**1**) open and are consistent with the quenching of the transient species seen in the laser photolysis of (**1b**).

These ylides should cleave preferentially, as anticipated in non-protic solvents, to aryl aldehydes and a heterocyclic fragment. We have not been successful in cleanly trapping the heterocyclic species with alkenes even when 2-naphthaldehyde (**7b**) can be isolated in 98% yield when the oxiran (**1b**) is irradiated in neat 2-methylbut-2-ene at 254 nm. In contrast, the heterocyclic carbene of an analogous structure generated by the photolysis of 3-diazo-1-methyloxindole is intercepted by alkenes.[11]

An attempt to create the oxopyrazoline carbene (**6a**) in an alternative and more conventional manner by the photolysis (350 nm)§ of 4-diazo-3-methyl-1-phenyl-5-oxo-2-pyrazoline (**8**)[12] in methanol yields two isomeric forms of methyl 3-phenylazo-2-butenoate (**9**).[13] A transient (τ >200 μs) is detected when (**8**) is subjected to laser flash photolysis (benzene or methanol, 22 °C), possibly implicating a ketene intermediate in this reaction. Alternatively, the azoesters may arise *via* the protonation[14] of the intermediate (**6**) with a concurrent opening of the ring by the nucleophilic solvent.



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† The validity of generalizations of this type is supported by *ab initio* SCF calculations using STO-3G and 4-31G basis sets and 3 × 3 CI described in K. N. Houk, N. G. Rondan, C. Santiago, C. J. Gallo, R. W. Gandour, and G. W. Griffin, *J. Am. Chem. Soc.*, 1980, **102**, 1504.

‡ Satisfactory elemental analyses for carbon, hydrogen, and nitrogen were obtained for all new compounds. Physical constants: 1,3-diphenyl-4-(2-naphthylidene)-5-oxo-2-pyrazoline, m.p. 136—137 °C, (**1a**), m.p. 79—80 °C, (**1b**), m.p. 140—141 °C, (**1c**), m.p. 150—168 °C (decomp.), (**1d**), m.p. 167—181 °C (decomp.), (**1e**), m.p. 164 °C (decomp.), *E*-(**9**), b.p. 95 °C (0·046 mmHg), *m/e* 204.

§ Irradiations were conducted in serum-capped quartz or Pyrex tubes employing a Rayonet RPR-100 chamber reactor equipped with 16 8W 254 nm or 350 nm lamps. Degassed solutions were stirred during irradiation. Irradiations were conducted at 40 °C unless otherwise noted.

Thus (**6**) is not trapped by alcohol in the usual manner.[11,14] That azoesters are not observed as products upon photolysis of the oxirans (**1b**) and (**1c**) suggests that fragmentation of the carbonyl ylides (**2b**) and (**2c**) in protic media into intermediates similar to (**6**) is precluded by their efficient interception by the solvent.

E.s.r. and optical spectroscopic, as well as further chemical and laser photolysis experiments, are underway to characterize more fully the unusual properties of the reactive intermediates derived from oxopyrazoline-4-spiro-oxirans and diazopyrazolinones.

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