

Photochemistry of Azoalkane: Formation of the Rearrangement Product by Photoinduced Electron Transfer of the Pyrazoline Derivative

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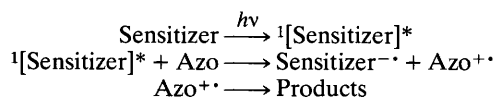
9,10-Dicyanoanthracene, DCA, sensitized decomposition of 3-methoxycarbonyl-4-phenyl-3,5,5-trimethyl-1-pyrazoline, **1**, leads to the cyclopropane derivative **2**, and the alkene **3**; compound **3** is a rearrangement product formed *via* a radical cation intermediate.

Following the report of the reaction of singlet excited azoalkane with CCl_4 ,¹ there has been interest in the behaviour of the radical cation of azoalkane, which is generated from the ground or excited state.^{2,3} Recently, the radical cation of 1,1'-azanorbornane was detected by spectroscopy.⁴ There are, however, few examples of photoinduced reactions, except for the Adam's rearrangement of tricyclic azo compounds.³ Now, we report the interaction between a singlet excited sensitizer and a pyrazoline derivative. An electron transfer from the pyrazoline derivative to the excited sensitizer initiates an interesting rearrangement reaction through the radical cation intermediate, which is shown in Scheme 1.

3-Methoxycarbonyl-4-phenyl-3,5,5-trimethyl-1-pyrazoline, **1**, was prepared from methyl- α -methyl cinnamate⁵ and

2-diazopropane⁶ as previously reported.⁷ In order to determine the behaviour of the 1,3-biradical, which is generated from **1**, the thermochemical and photochemical reactions of **1** were examined.

Thermolysis of neat **1** was performed; **1** was also photolysed using a 1 kW high-pressure mercury-arc lamp through a Pyrex filter, in acetonitrile. Heating and irradiation were continued until compound **1** disappeared (shown by HPLC). Products were isolated in each case and the structures were determined by ¹H, ¹³C NMR and mass spectra; the stereochemistry of **2** is uncertain, although we suspect that **2a** is produced stereospecifically on the basis of its sharp melting point and simple NMR spectrum, and also because of the lifetime of the 1,3-biradical generated from the decomposition of **1**. Yields are shown in Table 1.



Scheme 1

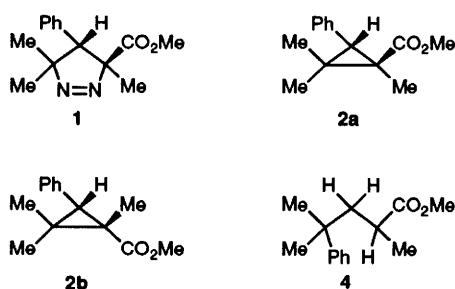
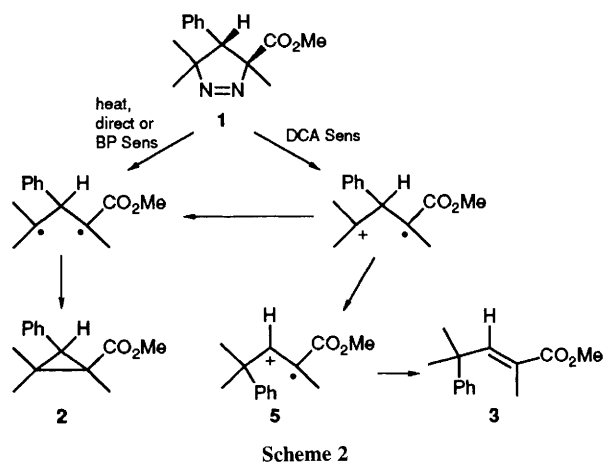


Table 1 Direct and sensitized photolysis and thermolysis of **1**

	Photolysis ^b			Thermolysis ^e at 140 °C
	Direct ^c	DCA sens ^d	BP sens ^d	
2	66	42	90	74
3	Trace	25	None	Trace

^a Conversions are 100% in all experiments. ^b In acetonitrile. ^c A solution of **1** (0.01 mol dm⁻³) was photolysed for 3 h under argon atmosphere. ^d A solution of **1** (0.01 mol dm⁻³) and DCA (0.2 mmol dm⁻³) or BP (0.05 mol dm⁻³) were photolysed for 21 and 3 h, respectively, under an argon atmosphere. ^e In vacuum condition neat **1** was heated for 3.5 h.



Pyrazoline derivatives decompose with loss of nitrogen, and generate 1,3-biradical intermediates.⁸ They immediately recombine and produce the corresponding cyclopropyl compounds. In the case of this compound it is certain that **1** reacts *via* the usual path in both thermolysis and direct photolysis.

In the presence of benzophenone (BP) ($E_T = 69 \text{ kcal mol}^{-1}$) **1** is efficiently decomposed in acetonitrile by 366 nm light from a 1 kW high-pressure mercury-arc lamp through a Toshiba UVD36B glass filter. But 9-fluorenone ($E_T = 50 \text{ kcal mol}^{-1}$) did not sensitize the decomposition of **1**. As with other azoalkanes, phosphorescence of **1** was not observed. From the results of these triplet sensitization reactions the triplet excited state of **1** must lie between 50 and 69 kcal mol⁻¹. It is known that E_T for many azoalkanes is *ca.* 55 kcal mol⁻¹,⁹ and the behaviour of **1** can be explained by a normal energy-transfer mechanism. In this reaction the only product is **2** as in the direct photolysis and the thermolysis, but the yield is high. The higher yield of **2** implies that the benzophenone sensitized reaction is cleaner than the direct photolysis and the thermolysis, as the starting materials were entirely decomposed in all experiments. Trace amounts of **3** are obtained in the direct photolysis and the thermolysis of **1**. This implies that a small amount of **2** was decomposed by direct irradiation or heating and **3** was produced. On the other hand, in the benzophenone sensitized condition, **2** did not decompose as it could not absorb 366 nm light, and it was obtained at high yield; compound **3** was absent.

Compound **1** was photolysed in acetonitrile by 405 nm light in the presence of 9,10-dicyanoanthracene, DCA, which is a well known electron acceptor sensitizer. **1** had no absorption band at >380 nm, therefore, only DCA can absorb the wavelength in this experiment. **1** was easily decomposed and this reaction must proceed *via* an electron-transfer mechanism. The fluorescence of DCA was quenched by **1** in acetonitrile, and the quenching rate constant, k_q , was $2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate is a little smaller than the diffusion control rate constant, but it is well explained by the redox potentials of **1** and DCA. The oxidation potential of **1** was measured by cyclic voltammetry (CV) and an irreversible wave was observed.† Its E^{ox} was 2.11 V vs. SCE in acetonitrile. E^{red} and $E_{0,0}$ of DCA are -0.89 and 2.86 eV, respectively,¹⁰ and a coulomb term, $e_0^2/\epsilon a$, is about 1.5 kcal mol⁻¹ in acetonitrile. From these values $\Delta G = +1.7 \text{ kcal mol}^{-1}$ is obtained using the Rehm-Weller equation: $\Delta G = E^{\text{ox}} - E^{\text{red}} - E_{0,0} - e_0^2/\epsilon a$.¹¹ The slow electron-transfer rate constant is predicted from this positive ΔG value, and

the range of k_q might be between 10^8 higher and $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ lower.¹¹ From this result we conclude that this reaction is caused by an electron transfer from **1** to singlet excited DCA. This reaction gave the very unique rearrangement product **3** in high yield together with the usual product **2**. Structure **3** is determined by ¹H, ¹³C NMR, and mass spectra. **3** was hydrogenated by palladium-carbon catalysis in order to confirm the structure, and **4** was obtained as expected. The DCA sensitized reaction of **2** was attempted, but no reaction occurred. From this result it is clear that **3** is the primary product of the DCA sensitized reaction of **1**. It is noteworthy that this compound is not observed in other reaction cases. The mechanism is not simple nitrogen loss but an electron-transfer mechanism, which includes nitrogen loss (Scheme 2).

Electron transfer from the pyrazoline **1** to the excited DCA oxidant affords the pyrazoline radical cation and DCA radical anion. Loss of molecular nitrogen generates the radical cation. Half of the radical cations engage in electron back-transfer with DCA radical anions leading to the 1,3-biradicals. It then recombines and produces the cyclopropane **2**. The remaining part of the radical cations undergo rearrangement; the phenyl moiety transfers to cation position, yielding the radical cation **5**. Subsequent electron transfer produces the alkene **3**. This rearrangement of the phenyl moiety is similar to the electrochemical oxidation reaction of aromatic alkenes.¹²

In addition to **1**, its *p*-methyl derivative [3-methoxycarbonyl-4-(*p*-tolyl)-3,5,5-trimethyl-1-pyrazoline: **6**] gave the alkene in high yield (56%) with the cyclopropane type product (15%), whereas **6** gave only cyclopropane on thermolysis and direct photolysis, as with **1**. The higher yield of alkene in the DCA sensitized photolysis of **6** than of **1** is readily explained on the basis of the mechanism shown in Scheme 2. The yield of the rearrangement product is presumed to be predominant by the nucleophilicity of rearrangement moiety and the rate of electron back-transfer, both influences are yet to be confirmed. The substituent effect on the phenyl moiety and the influence on yield of the rearrangement product by other sensitizers having different reduction abilities in the excited state, are currently being investigated.

It is usually difficult to confirm electron transfer reactions, especially in the case of azoalkane. In this experiment, the rearrangement product clearly indicates the presence of the radical cation intermediate generated by the photoinduced electron transfer.

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† Electrochemical potentials were measured by CV at a platinum electrode in dry acetonitrile with 0.1 mol dm⁻³ tetraethylammonium perchlorate as supporting electrode.