The Photolysis of 4-Alkylidene-Δ^1-pyrazolines: a Route to Trimethylenemethyls

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To rationalize the formation of the two methylenecyclopropanes (I and II; X = O.CO.Et) in the photolysis of the 4-alkylidene-Δ^1-pyrazoline (III; X = O.CO.Et) we suggested the intermediate (IV; X = O.CO.Et) of unspecified multiplicity.[1] The theoretically important[2] parent species, trimethylenemethyl (V), has recently been generated photolytically from 4-methylene-Δ^1-pyrazoline and found by e.s.r. spectroscopy to have a triplet ground-state,[3] in agreement with Hückel molecular orbital calculations.[4] There is also convincing evidence from deuterium isotope effects that trimethylenemethyl is an intermediate in the gas-phase thermolysis of 4-methylene-Δ^1-pyrazoline.[5] Species related to (V) have also been considered in connection with the rearrangement of methylenecyclopropanes;[6,7a] and a metal complex, trimethylenemethyliron tricarbonyl, has been prepared.[7b] In view of the current interest in this topic, we report here experiments which suggest that the photosensitized decomposition of 4-alkylidene-Δ^1-pyrazolines may be a general route to derivatives of trimethylenemethyl in the triplet state.

Pentane solutions of the pyrazolines (III; X = O.CO.Et)[1] and (III; X = Cl)[8] (λ_{max} 327 mμ, ϵ 200) were irradiated in Pyrex apparatus with a medium-pressure mercury lamp. The Table gives the results of direct photolysis and photosensitization by benzophenone in terms of product composition. Control experiments showed that the products, (I) and (II), were stable to irradiation in the presence or absence of benzophenone. For both pyrazolines, the direct and the photosensitized reaction thus lead to entirely different product ratios, the latter giving a much higher proportion of "rearranged" isomer (II). Following Zimmerman,[9] we have shown that singlet energy transfer from benzophenone cannot be significant. With 0·001 M-pyrazoline solutions and an estimated bimolecular diffusion rate constant in pentane at 35° of 3×10^{10} l./moles-sec., the unimolecular collision rate becomes 3×10^7 l./moles-sec., or 0·3% of the rate of intersystem crossing of singlet-excited benzophenone ($\sim 10^{10}$ sec.$^{-1}$). It is improbable that the sensitized reactions were the consequence of some specific chemical reaction between triplet benzophenone and the substrate, since photosensitized decomposition of the pyrazoline (III; X = Cl) (0·001 M) with triphenylene gave a very similar product ratio (I)/(II). (Triphenylene triplet has an excitation energy close to that of

TABLE

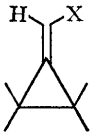
	Relative yields (%)[a] of methylenecyclopropanes	
	(I)	(II)
Direct photolysis		
(III; X = Cl)	77	23
(III; X = O.CO.Et)	64	36
Photosensitized (Ph_2CO)[b]		
(III; X = Cl)	25	75
(III; X = O.CO.Et)	18	82

[a] Averages of duplicate g.l.c. analyses of duplicate experiments (±1%). Overall yields of (I) plus (II) were *ca.* 90% for direct photolysis, *ca.* 80% for photosensitized reaction.

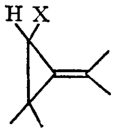
[b] The benzophenone absorbed 95—96% of the incident light. By-products derived from the solvent interfered with accurate g.l.c. analysis in experiments in which the benzophenone absorbed 99% of the incident light; *e.g.*, for (III; X = Cl), (I) and (II) were obtained in relative yields of 22—25 and 75—78% in such experiments.

benzophenone, but differs from benzophenone triplet in having the π, π^* configuration.[10])

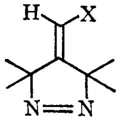
Photosensitization thus leads to triplet pyrazoline, and this then probably loses ground-state nitrogen to give the triplet (IV), which can cyclize in three ways. If purely statistical, this would lead to a (I)/(II) ratio of 1 : 2. The somewhat enhanced preference for the cyclopropane (II) must then be due to electronic, and possibly also steric, factors.



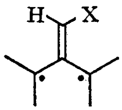
(I)



(II)

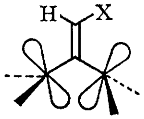


(III)

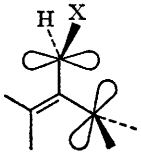


(IV)

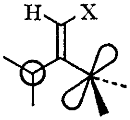

(V)



(VI)



(VII)



(VIII)

Direct photolysis appears to involve only singlet species, and not concurrent singlet and triplet reactions, since photolysis of compound (III; X = Cl) in 2·4 M-piperylene (an efficient triplet quencher[11]) gave the same (I)/(II) ratio as obtained in the unsensitized reaction in pentane alone. Also, we have been unable to detect *any* triplet species by e.s.r. spectroscopy, when the pyrazoline (III; X = Cl) was photolyzed in a variety of rigid media at 77°K. The simplest view of the singlet reaction (which is consistent with recent studies with other cyclic azo-compounds[12]) is that loss of nitrogen leads initially to the species (VI) for which σ-bond formation (giving I) is comparable in rate with the rotations required for the formation of singlet (IV),* or possibly with processes involving less delocalized species, *e.g.*, (VI) → (VII) either directly or *via* (VIII) (*cf.* ref. 6). The more nearly statistical result of the photosensitized reaction is then attributable to a triplet's longer life-span, which allows enough time for the most stable (planar) π-system to be reached efficiently.

Preliminary results with (III; X = Cl), using product ratio (I)/(II) as criterion of mechanism, show that with sensitizers having triplet excitation

* Our negative e.s.r. experiment cannot be taken as proof that the planar system (IV) is *not* involved in the direct photolysis of the pyrazolines. Nor is it at variance with Dowd's positive result for trimethylenemethyl (V);[3] for, unless the three arms of a molecule of this kind carry electronically identical groupings, [*e.g.*, $C(CXY)_3$, $C(CX_2)_3$] the degeneracy of the HMO's ψ_2 and ψ_3 is removed, and the molecule has a singlet ground-state.

energies (E_T) greater than *ca.* 65 kcal./mole triplet transfer is very efficient, whereas in the range *ca.* 55—65 kcal./mole it is of very variable efficiency, and gives intermediate values of the product ratio. In the low-energy range (E_T < 55 kcal./mole), the product ratio is *exactly* the same as that found for direct photolysis; and, with the exception of anthracene (E_T 42 kcal./mole; singlet energy transfer?) the reaction is very slow, being apparently due solely to the small fraction of the incident light absorbed directly by the pyrazoline.

Our current studies include attempts to trap analogues of (IV), and the thermolysis of alkylidenepyrazolines such as (III) (which also gives mixtures of two methylenecyclopropanes).

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