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INFLUENCE OF THE LOCALISATION OF THE EXCITATION ENERGY ON THE PHOTOCHEMISTRY OF α,β-EPOXYKETONES

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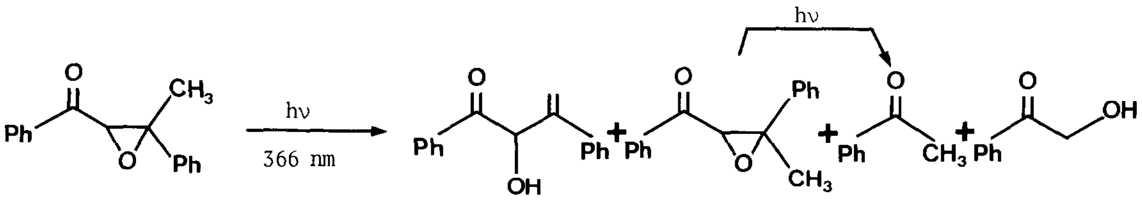
Irradiation at 366 nm of α-epoxyketones 8, 11, 12 in solution gave fragmentation to aldehydes and rearrangement either to β or α-diketones depending on the nature and localisation of the reactive triplet state in the starting molecule.

It has been shown that ylids are produced by irradiation of phenylepoxides (1), γ,δ-epoxy conjugated enones (2) and α,β epoxyketones (3). β-Diketones are usually the major products from the photolysis of α,β-epoxyketones (4) but epimerisation of the oxirane has been observed sometimes (5) and recent studies on optically active (E)-dypnone oxides 1 and (Z)-2-benzylidenecyclohexanone oxide 2 have shown that photoepimerisation leads to optically active products. Symmetrical intermediates are thus excluded and although C_α-O and C_β-O cleavage can explain the epimerisation of 1 and 2 respectively, it was interesting to see if a common process involving C-C bond breaking might be operating (6).

In order to determine if photoepimerisation and ylid formation are related and if these processes result from a $^3(\pi,\pi^*)$ excited state, we examined the photoreactivity of epoxyketones differing in the nature of the lowest triplet excited state and in the localisation of their excitation energy.

Excited arylketones are known to populate the triplet state with high efficiency (7). Epoxy ketones bearing a benzoyl group or an analog at one extremity of the oxirane should show similar behaviour, and we first verified that photochemistry of dypnone oxide 1 (8) involved the intermediacy of an excited triplet state. When 1 was irradiated at 366 nm in



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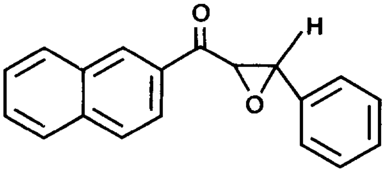
the presence of naphthalene (0,3 M) (E_T = 255 KJ) the whole reaction was efficiently quenched which suggested that 3 - 6 were formed from a triplet state. The phosphorescence spectrum of 1 showed vibrational structure characteristic of the $^3(n,\pi^*)$ state emission (E_T = 304 KJ). Although an ylid might be intermediate in the formation of acetophenone 5, the absence of a polarity effect when the reaction was carried out in different solvents (benzene, acetonitrile, methanol) leads to the conclusion that ylid formation was not a favoured pathway for excited dypnone oxides and that the low efficiency of the C-C bond cleavage from 1 was due to the (n,π^*) character of the lowest triplet excited state.

It was of interest to study the photochemistry of epoxyketones 7 and 8 for which the lowest triplet state should be $^3(\pi,\pi^*)$ (9). Unfortunatly no reaction except polymer



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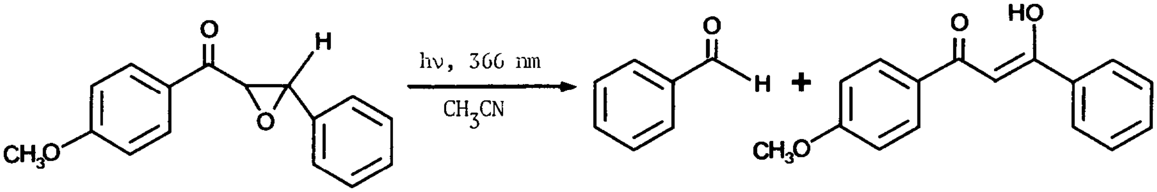
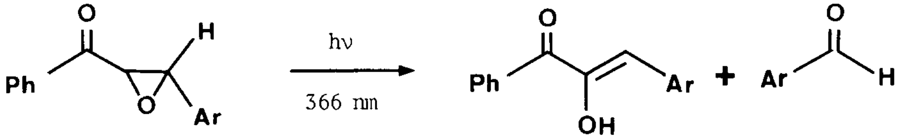


8 9 10

formation was observed when 7 was photolysed at 366 nm. The lack of reactivity might result from a too low energy level of the $^3(\pi,\pi^*)$ state (E_T = 245 kJ). However the emission of the naphthyl group was observed in the phosphorescence spectrum at 77°K indicating that the triplet energy is localized on this group and is not available for the isomerisation of the oxirane. In contrast, the β-diketone 10 (64%) and benzaldehyde 9 were formed during the irradiation of 8. In the phosphorescence spectrum of 8 at 77°K in 2-methyltetrahydrofuran the vibrational structure observed is in agreement with a $^3(n,\pi^*)$ state for T_1. The high yield of 10 suggested that $^3(n,\pi^*)$ might also be the lowest triplet state at room temperature in contrast to the case with p.methoxyacetophenone (9, 10). The traces of benzaldehyde 9 observed under these conditions might result from the fragmentation of an intermediate ylid.

In all the preceeding epoxyketones the excitation energy was localized on the ArCO group. We next examined epoxyketones 11 - 12 where the excitation energy can be transfered from an aroyl group to a naphthyl group fixed at the other extremity of the oxirane. Such a transfer did indeed occur in epoxyketones 11 and 12 as indicated by the characteristic naphthyl phosphorescence emission observed when 11 or 12 (10^{-5} M) in a 2-methyltetrahydrofuran glass at 77°K was irradiated at 366 nm in the benzoyl absorption band.

When either 11 (E_T = 249 kJ) or 12 (E_T = 253 kJ) was irradiated in solution at room temperature, an α-diketone and naphthaldehyde were the main products in the reaction mixture. Furthermore, the photolysis of 11 was quenched by t.piperylene (0.5 M) (E_T) = 248 kJ) and sensitized by benzophenone (E_T = 289 kJ) under conditions where all the light was absorbed by the sensitizer. This sensitization experiment allowed an energy transfer to the naphthyl group rather than to the benzoyl group and we can assume that α-diketones 13 and naphthaldehydes 14 were formed from a $^3(\pi,\pi^*)$ state of the starting epoxyketone. The high yield in aldehyde and the spectacular solvent effect suggest that a polar intermediate such as an ylid was formed and then decomposed to aldehyde (11).



			13	14
11	Ar = α-naphthyl	C_6H_6	17%	16%
		MeCN	8%	75%
12	Ar = β-naphthyl	MeCN	traces	79%

Since there is no photoepimerisation of the oxirane moiety of 10 or 11, there is no evident correlation between this process and aldehyde formation. Furthermore it appears that ylids are efficiently formed (12) from α-epoxyketones excited to the $^3(\pi,\pi^*)$ state when the excitation energy is localized on the β-arylsubstituent.

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