Tetrahedron Letters No. 29, pp 2727 - 2728.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0715-2727$02.00/0

CHARACTERIZATION OF YLIDS FORMED DURING THE PHOTOLYSIS OF α-EPOXYKETONES

Philippe Hallet, Jacques Muzart and Jean Pierre Pete[*]

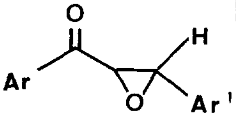
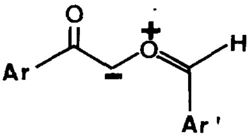
Laboratoire de Photochimie[†]
U.E.R. Sciences 51062 Reims (France)

The irradiation of α-epoxyketones 1 - 3 at 366 nm produced ylids which were characterized by their absorption spectra and by trapping with maleic anhydride.

In the preceeding paper, we have shown that aldehydes are produced during the irradiation of α-epoxyketones excited to their $^3(\pi,\pi^*)$ excited states (1). According to the work of Griffin and coworkers (2) on the photolysis of styryl epoxides, ylids should be intermediates for the formation of aldehydes in these irradiations. We now report that we have been able to detect ylids by their absorption spectra at low temperature and to trap them at 25°C when α-epoxyketones are photolyzed in the presence of various dipolarophiles.

When photolyzed at 77°K in a 2-methyltetrahydrofuran glass, epoxyketones led to coloured species which gave structureless visible spectra and were characterized by their absorption maxima (table). The coloured intermediates thus observed were stable for hours in the dark at 77°K. However, the irradiated samples were rapidly bleached when the temperature increased or when the coloured glass was irradiated with visible light at 77°K. We believe that ylids are the absorbing intermediates in the photolysis of these α-epoxyketones at low temperature (2, 3).

Table

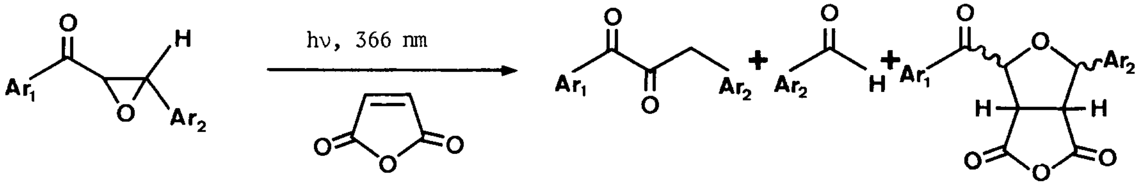
	E_T kJ.mol^{-1}	Emitting excited state	 λ_{max}
1	249	π,π^*	585 nm (navy blue)
2	253	π,π^*	560 nm (blue)
3	245	π,π^*	575 nm (blue)

[†] Equipe de Recherche Associée au C.N.R.S. n° 688.

When solutions of α-epoxyketones 1 - 3 were irradiated in the presence of maleic anhydride (4) cycloadducts (5), α-diketones and naphthaldehyde were obtained. Yields of the cycloadducts increased with increasing solvent polarity.

These results can be rationalized if we assume that the aldehyde and the adducts come from an ylid intermediate (6). To verify that products came from a $^3(\pi,\pi^*)$ state of the starting epoxyketone, we studied sensitization at 366 nm by benzophenone (E_T = 289 kJ): a similar reaction mixtures was obtained at room temperature while, in a 2-methyltetrahydrofuran glass, we detected the emission of the naphthylgroup and the blue colour characteristic of the ylid.

Scheme



	Ar$_1$	Ar$_2$	Solvent	Conversion %	5	6	7
1	Ph	α-naphthyl	MeCN	94	traces	43%	33%
			C_6H_{12}	75	-	87%	6%
			MeCN Ph$_2$CO	94	traces	15%	30%
2	Ph	β-naphthyl	MeCN	87	traces	34%	38%
3	β-naphthyl	β-naphthyl	MeCN	80	traces	25%	16%

References :

1) P. Hallet, J. Muzart and J.P. Pete, Tetrahedron Lett., preceeding communication and references therein.
2) N.R. Bertoniere and G.W. Griffin, Organic Photochem. III, Ed. Dekker, 120 (1973).
3) Recently coloured species have been detected under similar conditions from chalcone oxide and its 2-methoxyderivative cf. D.J. Dewar and R.G. Sutherland, J. Chem. Soc. Perkin II, 1523 (1977). We have shown that α-epoxyketones substituted by an arylgroup in the β position gave, in almost every case, a coloured species when irradiated at 77°K, even when ylids could not be trapped using various dipolarophiles.
4) Other dipolarophiles such as dimethylacetylenedicarboxylate,alkyl maleates and fumarates have also been used successfully (P. Hallet, to be published).
5) It has been reported very recently that methylacrylate cycloadds to the ylid derived from the photolysis of chalcone oxide. G.A. Lee, J. Org. Chem., 43, 4257 (1978).
6) When the stereochemistry of the adducts was determined, the reaction was seen to be stereospecific and the observed stereochemistry was in agreement with a disrotatory opening of the oxirane followed by stereospecific cycloaddition.

(Received in UK 18 May 1979)