The Addition of Azomethine Ylids to Diphenylcyclopropenone: Synthesis of Novel 4-Oxazolines

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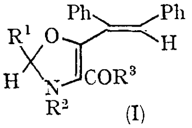
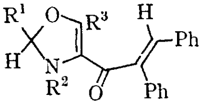
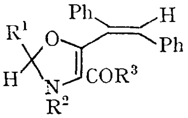
4-OXAZOLINES represent a hitherto unknown heterocyclic system, although they have been postulated as intermediates in the Lewis acid-catalysed rearrangement of 2-aroylaziridines, leading to the formation of oxazoles.[1] We report the preparation of 4-oxazolines by the addition of azomethine ylids, derived from acylaziridines, to diphenylcyclopropenone (DPP). Treatment of either *cis*- or *trans*-2-benzoyl-1-cyclohexyl-3-phenylaziridine[2] with one equivalent of DPP[3] in refluxing benzene, followed by chromatographic separation, affords the 4-oxazoline (I; $R^1 = R^3$ = Ph, $R^2 = C_6H_{11}$) (46·5%), m.p. 163°; ν_{max} ($CHCl_3$) 1695 cm.$^{-1}$ (C=O); δ_{Me_4Si}($CDCl_3$) 2·8—3·1 (m, 1H), 1·8—0·4 (m, 10H, cyclohexyl protons), 4·95 (s, 1H, 2-H), and 8·0—6·7 (m, 21H, aromatic protons and vinyl proton), *M* (mass spectrum) 511·2510; calc. 511·2511. The 1695 cm.$^{-1}$ absorption characteristic of aromatic ketones[4] supports (I) and discounts an alternative structure (II) which would display a carbonyl at 1665—1685 cm.$^{-1}$ (conjugated $\alpha\beta$-unsaturated ketone)[4c] Similarly, structure (III) is rejected on mechanistic grounds since nucleophile-catalysed opening of the diphenylcyclopropenone is *cis*,[3] and structure (IV) is rejected as its n.m.r. spectrum would show the 4-oxazolidine proton. Similar 4-oxazolines are obtained when the 1-aziridine substituent is replaced by Me and Me$_2$CH-; in the latter case the isopropyl methyl groups are non-equivalent, indicating proximity to an asymmetric centre, in accordance with structure (Ie) (see Table) (23·5%), m.p. 175°, $\nu_{\max}$ (CHCl$_3$) 1700 cm.$^{-1}$ (C=O), $\delta_{\text{Me}_4\text{Si}}$ (CDCl$_3$): 0·78 and 0·81 (overlapping d, *J* 6·5 Hz), 3·45 (m, 1H, *CH*Me$_2$), 4·96 (s, 1H, 2-H), and 8·1—6·8 (m, 21H, ArH and vinyl H) *M* 471. These 4-oxazolines display marked reversible thermochromism and photochromism to red species, and all give bright red melts, which are



(I)



(II)



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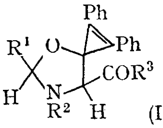
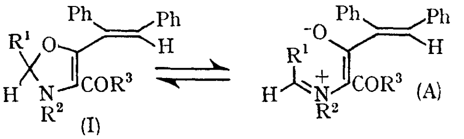


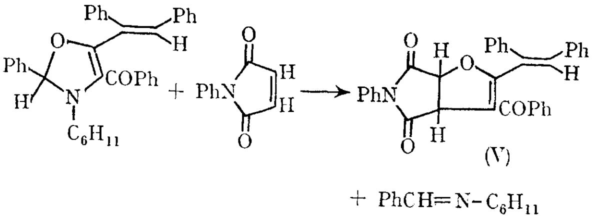
(IV)

tentatively attributed to the following equilibrium.



4-Oxazoline (colourless) Azomethine ylid (red)

This phenomenon is reminiscent of the reversible thermochromism in some 1,3-dipolar addition products of azomethine imines[5] and of the ring chain isomerism exhibited by 3-acyl- (or 3-alkoxycarbonyl-) 2-biphenylenyl-2,3-dihydro-1,3,4-oxadiazoles.[6] In support of the proposed equilibrium (A) and as expected for the ylid structure, the compounds are stable to alkali. The oxazoline (I) reacts with *N*-phenylmaleimide with extrusion of the anil moiety to give (V), (65%), m.p. 222—224° $\nu_{\max}$ (CHCl$_3$) 1695 (aromatic C=O),[4] and 1725 cm.$^{-1}$ (imide C=O)[4b], $\delta_{\text{Me}_4\text{Si}}$ (CDCl$_3$) 8·1—6·8 (m, 21H, ArH and vinyl H), and AB quartet centred at 4·05 and 4·16 (*J* 9·2 Hz) (2H, bridgehead protons), *M* (mass spectrum) 511·1783, calc. 511·1784. The orientation of the furan side-chains follows from the structure of the 4-oxazoline and is confirmed by the aryl ketone i.r. absorption and strong peaks at *m/e* 105 (PhCO-) and its counter-ion. The observed reaction of DPP with azomethine ylids to produce 4-oxazolines is in marked contrast to that with other 1,3-dipoles,



4-*Oxazolines*†

No.	R^1	R^2	R^3	M.p.	Yield (%)	Mol. Ion
(I)	Ph	C$_6$H$_{11}$	Ph	163°	46·5	511
(Ia)	*p*-MeO·C$_6$H$_4$	C$_6$H$_{11}$	Ph	158—160°	23	541
(Ib)	*m*-NO$_2$·C$_6$H$_4$	C$_6$H$_{11}$	Ph	165—167°	27	556
(Ic)	Ph	C$_6$H$_{11}$	*p*-NO$_2$·C$_6$H$_4$	191·5—192·5°	5	556
(Id)	Ph	C$_6$H$_{11}$	*p*-MeC$_6$H$_4$	175—176°	20	525
(Ie)	Ph	Me$_2$CH	Ph	175°	23·5	471
(If)	Ph	Me$_2$CH	*p*-MeC$_6$H$_4$	165—166°	31	485
(Ig)	Ph	Me	Ph	145°	20	443

† (Satisfactory analytical data were obtained on all new compounds).

e.g. diazomethane where primary addition occurs at the carbon–carbon double bond.[7]

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